Electrochemical methods for monitoring the content of polysulfides in environmental objects

O S Aksinenko\textsuperscript{1}, S V Kovaleva\textsuperscript{1} and A V Korshunov\textsuperscript{2}

\textsuperscript{1}Department of Chemistry and Methods of Teaching Chemistry, Tomsk State Pedagogical University, Tomsk, 634061 Russia
\textsuperscript{2}Department of Building Materials and Materials Science, Moscow State University of Civil Engineering, Moscow, 129337 Russia

\textsuperscript{2}E-mail: korshunovav@mgsu.ru
Stability of polysulfides in aqueous solutions

Figure 1. Calculated dependences of logarithms of equilibrium activities for ion-molecular species on potential (s. h. e.) for system S–H₂O (except SO₄²⁻) at pH 7.5 (a) and 13 (b) (25 °C; [S]ₜₒₜ=0.1 M)

Polysulfides are relatively stable in narrow pH and potential ranges: in an acidic environment, sulfanes quickly decompose to form sulfur and hydrogen sulfide; in an alkaline environment, low-molecular-weight species are stable. In the presence of even low-level oxidizing agents, polysulfides are quickly oxidized to form numerous oxygen-containing compounds.
Speciation of sulfur in the presence of Hg

Fig. 2. Calculated diagrams of the equilibrium activities of ion-molecular species on potential (s. h. e.) in the system Hg–S–H₂O (except SO₄²⁻) at pH 7.5 (a) and 13 (b) (25 °C; total [Hg]=1·10⁻⁵ M and [S]=0.1 M)

Due to the high affinity of mercury to sulfur, the predominant equilibrium phase in the system in a wide pH range is poorly soluble HgS, the region of thermodynamic stability potentials of which overlaps the region of polysulfide potentials
Cathodic stripping voltammetry of polysulfides with Hg-film electrode

**Fig. 3.** Direct- (a) and alternating-current (b) voltammograms of HgFE in alkaline solutions (supporting electrolyte 0.1 M NaOH) at different concentrations of sodium disulfide: 1) $4 \cdot 10^{-7}$, 2) $6 \cdot 10^{-7}$, 3) $8 \cdot 10^{-7}$, 4) $1.2 \cdot 10^{-6}$, 5) $1.6 \cdot 10^{-6}$, 6) $4 \cdot 10^{-7}$, 7) $6 \cdot 10^{-7}$, 8) $8 \cdot 10^{-7}$, 9) $1 \cdot 10^{-6}$ M ($E_{\text{init}} = -0.5$ V; $E_{\text{end}} = -1.1$ V; $w=40$ mV/s; $\Delta U=3$ mV; $\theta=0^\circ$; $f=25$ Hz)
Summary

• The main products during the oxidation of polysulfides at Hg-film electrode in an alkaline medium (pH=13), regardless the composition of the initial solution, are HgS and S, the subsequent cathodic reduction of which allows to quantify the total content of sulfide and polysulfide species in a solution, as well as average polysulfidity in $S_n^{2-}$ ions.

• Optimal conditions to determine polysulfide ions $S_2^{2-}$ and $S_3^{2-}$ in an alkaline medium (0.1 M NaOH) at HgFE using direct- and alternating current cathodic stripping voltammetry were established: preliminary deaeration of solutions with nitrogen; preelectrolysis potential $-0.5$ V (sat. Ag/AgCl/KCl); duration of preelectrolysis 1–2 min; subsequent cathodic polarization to $E=-1.0$ V.

• Under these conditions, the concentration dependence of cathode current $I_{\text{cat}}$ at $E_{\text{max}}=-0.8\div-0.9$ V is linear in the range of polysulfide concentrations $1\cdot10^{-7}\div1\cdot10^{-3}$ M. The method can be used to determine the total content of polysulfides in solutions and to calculate the average degree of polysulfidity in $S_n^{2-}$ ions.