Electrochemical methods for monitoring the content of polysulfides in environmental objects

O S Aksinenko¹, S V Kovaleva¹ and A V Korshunov²

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

²E-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) 4·10^{-7}, 2) 6·10^{-7}, 3) 8·10^{-7}, 4) 1.2·10^{-6}, 5) 1.6·10^{-6}, 6) 4·10^{-7}, 7) 6·10^{-7}, 8) 8·10^{-7}, 9) 1·10^{-6} M

\(E_{\text{init}}=–0.5 \text{ V; } E_{\text{end}}=–1.1 \text{ V; } \omega=40 \text{ mV/s; } \Delta U=3 \text{ mV; } \theta=0^\circ; f=25 \text{ Hz}\)
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; pre-electrolysis potential $-0.5$ V (sat. Ag/AgCl/KCl); duration of pre-electrolysis 1–2 min; subsequent cathodic polarization to $E=-1.0$ V.

• Under these conditions, the concentration dependence of cathode current $I_{\text{cat}}$ at $E_{\max}=-0.8$–$-0.9$ V is linear in the range of polysulfide concentrations $1\cdot10^{-7}$–$1\cdot10^{-3}$ 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.