Chelate adsorption for trace voltammetric measurements of iron(III)

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Introduction

The determination of iron in a variety of media has been hampered by a lack of sufficiently sensitive analytical methods. The redox reactions of iron(II) and iron(III) species permit their convenient polarographic measurement. DC polarography [1, 2], differential pulse polarography [3], and AC polarography [4] have been used for this purpose, allowing quantitation at the millimolar and sub-micromolar concentration levels using short preconcentration times. The limit of detection after 1 min preconcentration is 0.04 µg l⁻¹ (7 × 10⁻¹⁰ M), and the relative standard deviation at the 10⁻⁷ M level is 4.7%. The effects of possible interferences, due to coexisting metal ions or organic surfactants, are evaluated. The ability of measuring iron(III) in the presence of iron(II) is illustrated. Actual analyses of sea and tap waters are reported.

Experimental

Apparatus and reagents

The equipment used to obtain the voltammograms, an EG & G PAR 264 A voltammetric analyzer with a PAR 303 static mercury drop electrode, was described in detail previously [14, 15]. A medium-size drop with a surface area of 0.015 cm² was used. Ag/AgCl (3 M KCl) reference electrode and a platinum wire auxiliary electrode were employed. All solutions were prepared from double-distilled water. The iron(III) stock solution (1000 ppm) was prepared from FeCl₃·6H₂O. Solochrome Violet RS (SVRS) and...
other dyes were purchased from Aldrich; a stock solution of the dye, \(1 \times 10^{-4} \text{ M}\), was prepared daily. Supporting electrolyte was acetate buffer (pH 5.1). Sea water was unfiltered surface water collected at San Diego (CA) and stored frozen. Tap water was collected directly from the laboratory tap.

**Procedure**

Ten ml of the supporting electrolyte solution, containing \(1.5 \times 10^{-6} \text{ M}\) of SVRS were pipetted into the cell, and degassed with nitrogen for 8 min. The preconcentration potential (usually \(-0.40 \text{ V}\)) was applied to a fresh mercury drop while the solution was stirred (400 rpm). Following the preconcentration period, the stirring was stopped and after 15 s the voltammogram was recorded by applying a negative going linear potential scan. The scan was terminated at \(-1.10 \text{ V}\). After background stripping voltammograms were obtained, aliquots of the iron(III) standards were introduced. A new drop was extruded at the beginning of each preconcentration period. Throughout this operation, nitrogen was passed over the solution surface. All data were obtained at room temperature.

**Results and discussion**

**Response characteristics and optimization**

Figure 1 shows repetitive cyclic voltammograms for SVRS-containing acetate buffer solutions in the absence (a) and presence (b, c) of iron(III). When the dye-containing solution was stirred for 1 min while the electrode held at \(-0.32 \text{ V}\) prior to the scan, a large cathodic peak associated with the reduction of the adsorbed dye is observed at \(-0.42 \text{ V}\) (a). Subsequent scans result in a sharp decrease of the dye peak, to a stable response associated with the solution-phase species (i.e., rapid desorption of the reduced form of the dye). No peaks are observed upon scanning in the positive direction. When the same experiment is repeated after addition of \(10 \mu\text{g/l}\) iron(III), an additional peak associated with the reduction of the Fe/SVRS chelate is observed at \(-0.70 \text{ V}\) (b). An increase of the chelate peak is observed upon changing the potential scan rate on the positive direction. When the same experiment is repeated after addition of \(10 \mu\text{g/l}\) iron(III), an additional peak associated with the reduction of the Fe/SVRS chelate is observed at \(-0.70 \text{ V}\) (b). An increase of the chelate peak is observed upon changing the preconcentration potential to \(-0.42 \text{ V}\) (c). Such behaviour is attributed to reduced competition by the free dye on the surface sites (as supported also by the effect of the preconcentration potential described below). A rapid desorption of the chelate is indicated from the sharp decrease of its peak observed in subsequent scans. Using \(25 \mu\text{g/l}\) iron(III), \(2.5 \times 10^{-6} \text{ M}\) SVRS, and stirring at \(-0.40 \text{ V}\), maximum adsorption density was attained following 120 s. The maximum charge obtained by integrating the area under the stripping peak ("cut and weigh" method), was found to be \(0.8 \mu\text{C}\). Division of the charge by the conversion factor (\(nFA\)) yields an adsorbed layer of \(1.3 \times 10^{-16} \text{ mol/cm}^2\) (\(n = 4\)). Because of the mixed adsorbed layer the area occupied by a single chelate molecule cannot be estimated. The effect of potential scan rate on the peak current and potential was evaluated at maximum adsorption density. The Fe/SVRS peak was directly proportional to the scan rate. The plot of log (peak current) versus log (scan rate) was linear, with a slope of 0.992 (standard deviation of the slope, 0.03; correlation coefficient, 0.999), over the \(10-100 \text{ mV/s}\) range. A slope of 1.000 is expected for an ideal redox reaction of surface-bound species. A negative shift in the peak potential, from \(-0.67 \text{ V}\) to \(-0.73 \text{ V}\), was observed upon increasing the scan rate from 10 to 200 mV/s.

The interfacial and redox behaviours of the Fe/SVRS chelate can be utilized for trace measurements of iron(III) by means of adsorptive stripping voltammetry. For example, Fig. 2 illustrates typical voltammograms for \(2.5 \mu\text{g/l}\) (\(4.5 \times 10^{-8} \text{ M}\) Fe(III) in the presence of \(1.5 \times 10^{-6} \text{ M}\) SVRS, following different preconcentration periods: 0(a), 30(b), 60(c), and 120(d) s. Well-defined peaks are observed at the \(\mu\text{g/l}\) level, using short preconcentration times. The peak width at half-height is 42 mV. The peak increases with increasing preconcentration time, indicating an enhancement of the chelate concentration at the mercury surface. One and 2-min preconcentrations result in 6- and 9-fold enhancements, respectively, of the response without preconcentration. Also shown in Fig. 2 are (peak current) vs. (preconcentration time) plots for 2.5 and 5 \(\mu\text{g/l}\) iron(III). As the preconcentration period increases, the peak current rises rapidly at first and then more slowly. Obviously, a trade-off between sensitivity and speed is advisable when optimizing the preconcentration time with 10 and 60 s suffice for convenient measurements at the 10 and 1 \(\mu\text{g/l}\) levels, respectively.