Experiment 14: Stability of Dithizone by Cyclic Voltammetry

SYNOPSIS:

Cyclic voltammetry will be used to investigate the reduction of dithizone which can occur during the UV-Vis dithizone based determination of lead. The goal will be to develop a sense of how cyclic voltammetry can be used to understand the kinetics of electron transfer reactions.

Readings Attached are some articles that describe the reaction of dithizone in solution with ferricyanide, and the cyclic voltammetry of dithizone.

Solutions

solvent: 20% ethanol; 0.2 M Na_2SO_4; 1 M NaOH	
dithizone:	$5x10^{-4}$ M in solvent
$Fe(CN)_6^{3-}$:	1 mM in solvent
broth:	$5x10^{-4}$ M dithizone and 1 mM $Fe(CN)_6^{3-}$ in solvent

Make up a salt/solvent solution
Make up a 1 mM dithizone solution in the salt/solvent

Equipment

PAR....
SCE reference electrode
Glassy Carbon electrode

Procedure

A. Reversible Cyclic Voltammograms

1. Polish the Pt electrode by pressing firmly down onto polishing wheel. Sonicate the electrode to remove any alumina used in polishing.
2. Set the waveform generator to sweep from +0.6 to -0.2 V at a scan rate of 50 mV/s.
3. Insert electrode in N_2 purged NaCl solution and take a **background** scan.
4. Transfer electrodes to N_2 purged $Fe(CN)_6^{3-}$ solution and take 5 single scans at 50 mV/s.
5. Repolish the electrode and take a single scan at 25 mV/s, 50mV/s, 100 mV/s, 200 mv/S, 500 mV/s, 1 V/s, 2 V/s, 100 V/s, 200 V/s.
6. Repolish the electrode and take three scans at 100 mV/s.

7. For each scan determine: cathodic peak potential and height (baseline subtracted), and anodic peak potential and height (baseline subtracted).

B. Kinetics of Compound Degradation: Dithizone

1. Purge electrolyte and electrolyte + Dithizone solutions
2. Polish electrodes as in A. above
3. Repeat scanning procedure as in A. above, with potential limits set from -0.5 to +0.5 V vs SCE.

C. Effect of $Fe(CN)_6^{3-}$ on Dithizone Degradation

1. Add $Fe(CN)_6^{3-}$ to your solution and repeat experiment B.

REPORT

In addition to the usually procedure, methods, figures, and data analysis discuss in essay format the following questions.

1. Make a plot of square root of scan rate vs baseline subtracted peak height for $Fe(CN)_6^{3-}$ reduction. Is the plot linear and what is the implication of a linear plot?

   The peak height is measured from the extrapolated baseline. For the reduction peak extrapolate your baseline from the more positive potential to a more negative potential. For the oxidative peak height take your baseline starting from the high current at the negative potential.
2. Make a plot of I_{pc}/I_{pa} for $Fe(CN)_6^{3-}$ as a function of scan rate. Is the plot linear and what does this tell you about the what in which the compound accommodates an electron?
3. For your 100 mV/s scan rate which you did three times, how precise is your ability to measure peak height (compute the relative standard deviation from three tries.)?
4. What role might your polishing procedure play on the your measurement?
5. For dithizone makes plots as in questions 1 and 2. What do these plots tell you about the stability of dithizone?
6. How is the stability affected by the presence of $Fe(CN)_6^{3-}$?
7. Comment on the implications of these results for the accuracy of the dithizone extraction method for the **quantitative** determination of lead.
8. Calculate the free energy of of the reaction of between $Fe(CN)_6^{3-}$ and dithizone based on the difference in the standard potentials.