

## SHORT COMMUNICATION

### AN INFRARED STUDY OF THIOCYANATE AT THE MERCURY ELECTRODE INTERFACE

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FTIR surface infrared spectroscopy of the mercury solution interface shows the adsorption of complex ions of mercury thiocyanate at potentials more positive than -200mV vs SCE, and indicates that thiocyanate ion is adsorbed by electrostatic physisorption at more negative potentials.

#### Introduction

We have recently reported vibrational spectroscopic data for species adsorbed at the mercury electrode(1). In that work, the species of interest was the strongly adsorbed isoquinoline system. An important observation in that work was that shifting of the vibrational bands was small compared to those observed at solid d-electron transition metal electrodes; the relative intensities of the bands for the adsorbed and solution species were markedly different as expected. We report in this work the surface infrared spectroscopy for adsorbed thiocyanate ion at the mercury-aqueous solution interface, and the spectral characteristics of the products of the electro-oxidation of mercury in the presence of thiocyanate ion.

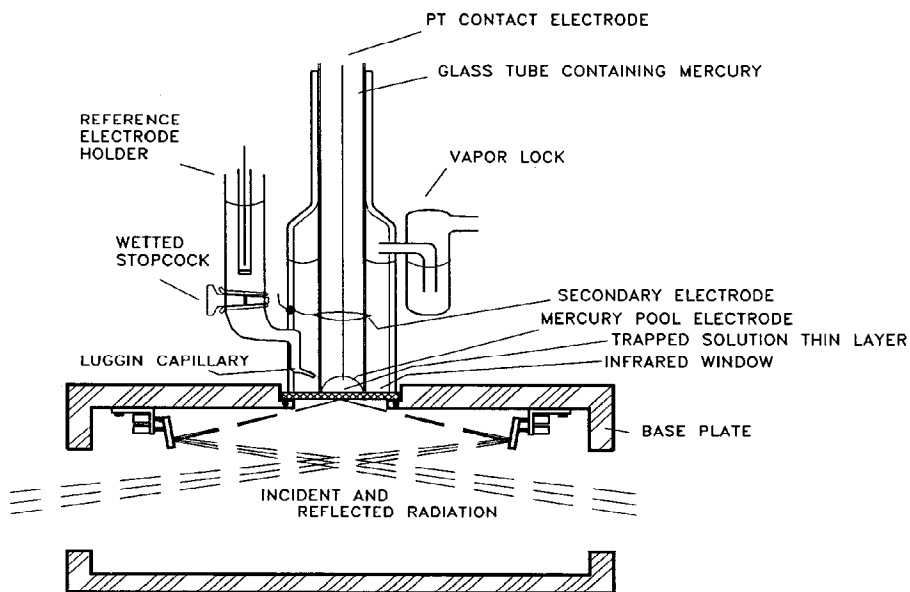


Figure 1. The Mercury Spectroelectrochemical Cell and Configuration

### Experimental

Infrared vibrational spectra of the mercury-solution interface were collected using the SNIFTIRS method, the theory and implementation of which have been described in detail elsewhere (2-4). A Bruker-IBM IR-98 infrared spectrometer was used for all measurements.

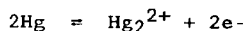
The electrochemical cell was constructed from a glass syringe and holder as described previously (4) and modified so as to allow the cell to be mounted vertically above the spectrometer sample compartment (Figure 1). A glass tube, positioned against an infrared transparent window at one end of the cell, was filled to a height of a few millimeters with mercury which formed the working electrode. A thin layer of solution was trapped between the mercury electrode and the window (1). A platinum wire was inserted inside the tube to make contact to the mercury. The cell was mounted so that the window rested on an O-ring on the top of the spectrometer housing. A gas tight seal was formed when the spectrometer was brought under vacuum. Two gold mirrors were used to divert the infrared beam and focus it onto the mercury interface and collect the reflected beam. The angle of incidence at the electrode was set to 65°.

Solutions were prepared from triply distilled water (first from alkaline  $\text{KMnO}_4$ ). The mercury was triply distilled (American Scientific) and AnalaR grade  $\text{NaSCN}$  (Aldrich) and  $\text{NaF}$  (Fisher Scientific) were used without further purification.

All measurements were performed in solutions deaerated with argon. Electrochemical potentials are reported with respect to the saturated calomel electrode (SCE). All glassware was cleaned in a 50:50 mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , rinsed with triply distilled water, and steamed for 30 minutes before each experiment.

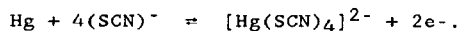
### Results and discussion

Reaction of thiocyanate at the mercury electrode was first studied by Kolthoff and Miller (5). In the absence of any adsorbates, the anodic oxidation of mercury in simple solutions proceeded as expected according to the reaction:



When thiocyanate was present, complex ions of the type  $[\text{Hg}(\text{SCN})_j]^{2-j}$  were reported to form at the surface upon electro-oxidation of mercury (6). Anson and Payne (7) have investigated the interaction of thiocyanate with a mercury electrode using chronocoulometry. These authors predicted that  $\text{Hg}(\text{SCN})_2$  was the primary product of the electrooxidation of mercury when thiocyanate is present at concentrations of 2 mM. A more recent study of the behavior of thiocyanate at a mercury electrode was undertaken by Dhaneshwar and Palrecha (8). These authors confirm the findings of Anson and Payne and suggest formation of  $[\text{Hg}(\text{SCN})_4]^{2-}$  when the thiocyanate concentration exceeds 4 mM.

We have investigated the interaction of thiocyanate at a mercury electrode at high (100 mM) concentrations of thiocyanate. Infrared spectra which reflect potential dependent processes at the mercury/solution interface are shown in Figure 2. These spectra were recorded at a base potential of -800 mV, near the potential of zero charge for the system (9). There are two potential regions of interest: that between -800 mV and -200 mV, where surface thiocyanate difference infrared absorption bands are absent, and the region more positive than -200 mV, where bands due to thiocyanate complexes appear. In the latter potential region, bands at  $2065\text{ cm}^{-1}$  and  $2116\text{ cm}^{-1}$  are assigned to the C-N stretching mode of solution free thiocyanate and  $[\text{Hg}(\text{SCN})_4]^{2-}$  species respectively (10-12). This region corresponds to the onset of mercury oxidation; the following reaction is suggested:



Further reaction of  $[\text{Hg}(\text{SCN})_4]^{2-}$  with the mercury electrode to form  $\text{Hg}_2(\text{SCN})_2$  has been suggested to explain the irreversible electrochemistry observed by Dhaneshwar and Palrecha for  $\text{SCN}^-$  concentrations above 4mM (8). At the high concentrations used in this work,

however, the magnitude of the equilibrium constants (7) suggests that formation of  $\text{Hg}_2(\text{SCN})_2$  is unlikely. Further, only bands due to  $[\text{Hg}(\text{SCN})_4]^{2-}$  appear in the spectra. Thus, we conclude that in 100 mM thiocyanate solutions,  $[\text{Hg}(\text{SCN})_4]^{2-}$  is the primary reaction product of the electro-oxidation of mercury.

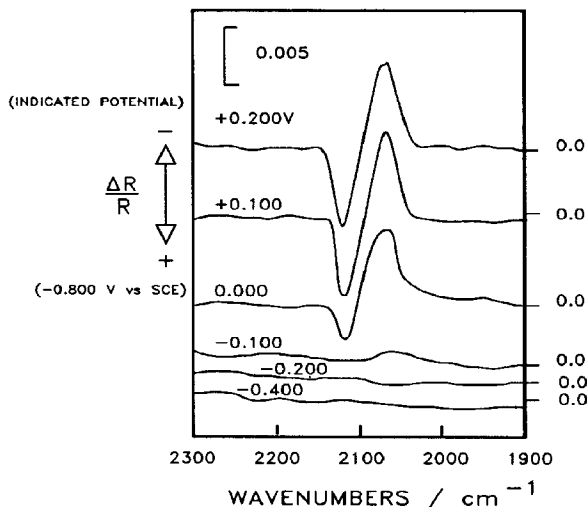


Figure 2. SNIFTIRS reflectance infrared spectra of 100mM NaSCN in 0.5M NaF at the mercury electrode as a function of potential.

As mentioned, we observe no difference SNIFTIRS infrared bands in the potential region between -800 mV and -200 mV vs SCE. Electrochemical measurements, however, clearly suggest adsorption of thiocyanate at the ( $\text{Hg}^{2+}$  free) mercury surface at potentials between -600 mV and -200 mV (7,9, and confirmed in this work). In addition, polarization modulation of the mercury-solution interface shows a weak surface band centered at about  $2090\text{ cm}^{-1}$ . The vibrational spectroelectrochemical measurements made in this work indicate that there is no change in interfacial thiocyanate concentration in this potential range. Further, there are apparently no potential dependent changes in the spectra of thiocyanate adsorbed on mercury which correspond to those observed for adsorbates on transition d-electron metals (e.g. CO,  $\text{CN}^-$ , and  $\text{SCN}^-$  on d-type (Pt, Ag, Au) metal electrodes (13-15)) (potential dependent changes in the  $2090\text{ cm}^{-1}$  band would give rise to difference spectra in the SNIFTIRS measurements). Since mercury has a closed shell electron configuration, a ligand-metal backbonding type interaction between  $\text{SCN}^-$  and the mercury surface is unlikely. Instead, strong physisorption is more likely. As the potential is made more positive, thiocyanate is probably more strongly bound by electrostatic interactions with the mercury surface, but this type of interaction will probably not perturb the structure of the thiocyanate species enough to give rise to a change in the vibrational spectrum. This can certainly occur when there is a bonding type interaction with the surface. We have shown that similar types of strong electrostatic or dipole-dipole non-bonding interactions are not generally strong enough to

change the vibrational characteristics of the system (17). These results also suggest that the field in the electrical double layer in this experiment may not be sufficiently intense to affect the oscillator strength of the adsorbed species.

We are presently investigating the use of various two- and three-body interaction theoretical models to this system. These models are capable of predicting the vibrational structure of the electrode solution interface, and have been quite successful when applied to adsorption phenomena at d-metal electrodes. We anticipate that generation of appropriate potential energy surfaces for the mercury-solution interface will give information regarding the dominant modes of surface interactions for species that have only certain possible mechanisms of binding to metal surfaces. We are comparing the vibrational results for a given species ( $\text{SCN}^-$ , isoquinoline, etc.) at different (d- and s-) metals and with different electrolytes, and will report those results elsewhere.

#### Acknowledgement

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