

Preliminary note

THE SPECIFIC ADSORPTION OF ANIONS ON A Hg-Pt OPTICALLY TRANSPARENT ELECTRODE BY TRANSMISSION SPECTROELECTROCHEMISTRY

WILLIAM R. HEINEMAN and JOHN F. GOELZ

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)

(Received 20th February 1978)

INTRODUCTION

Optical techniques have been applied with substantial success to the study of adsorption phenomena at electrode surfaces. Reflection techniques such as ellipsometry [1–3], specular reflectance spectroscopy [4–6], and internal reflection spectroscopy [4, 8, 9] have been used extensively. Recently, transmission spectroscopy through evaporated silver films has been found to be sensitive to adsorbed sulfate ions [7]. The light scattering techniques of Raman and Resonance Raman have recently been shown to exhibit remarkable sensitivity to adsorbed molecules [10–12]. These optical methods have been used to observe adsorbed species either directly via electronic and vibration/rotational spectroscopic transitions or indirectly by optical signals resulting from changes in optical constants in the interfacial region.

This preliminary note explores the potentiality of studying adsorption phenomena by transmission spectroelectrochemistry at Optically Transparent Electrodes (OTEs). The development and characterization of OTEs consisting of thin mercury films electrochemically deposited on platinum and carbon OTEs have been reported [13–15]. Optical changes observed by transmittance spectroscopy at the Hg-Pt OTE during potential step experiments have been observed and postulated to be caused by specific adsorption [14]. We report here results of experiments which indicate that transmission spectroscopy is a viable technique for observing the specific adsorption of anions at mercury optically transparent electrodes.

EXPERIMENTAL

Apparatus

The optically transparent electrochemical cell was constructed from lucite as previously described [14]. The cell was modified so that the electrode area was reduced to 3 mm². The total volume of solution required was ca. 1 ml. The OTE was vapor deposited platinum on glass microscope slides; the thickness of

the platinum ranged from 100 to 300 Å [16]. All potential measurements were made versus a saturated calomel electrode which was isolated from the solution via a vycor plug. The auxiliary electrode was a coiled platinum wire.

A Princeton Applied Research Model 175 Universal Programmer together with a Princeton Applied Research Model 173 Potentiostat and Model 179 Digital Coulometer was used to control the potential of the working electrode.

Absorbance changes at a single wavelength, 525 nm, were monitored in a spectrophotometer consisting of a tungsten quartz halide lamp (Lucas Power-bulb 453, 12V, 55W, England) powered by a 12V, 8A, D.C. Power Supply, a Schoeffel GM 100 miniature grating monochromator, and an Emitronics T124 Photomultiplier Tube (Gencom Division, Plainview, NJ) powered by a Fluka 412B High Voltage Supply. The current from the PMT was converted to voltage and amplified by a factor of ten with operational amplifiers (Teledyne Philbrick, 1026). The voltage output was monitored with a Fluka 8000A Digital Multimeter or a Digitec 261 digital VOM. A Hi-Tek Multipurpose Signal Averager Type A.A.1 (England) was used to collect transmittance-time data. The PAR 175 and the signal averager were simultaneously triggered by a Heath Digital Timing Module (Model EU 801-13). A Tektronix Dual Beam with Timing Module and Storage, Model 5103N Oscilloscope was used to preset the timing. System response signals from the signal averager were recorded on a Houston Instruments 2200-5-6 x-y recorder with time base.

Reagents

The solution used for deposition of mercury onto the platinum was a $2 \times 10^{-3} \text{ mol l}^{-1} \text{ HgNO}_3 \cdot \text{H}_2\text{O}$ (Baker, Analyzed) in $0.12 \text{ mol l}^{-1} \text{ HClO}_4$. The solutions used for the adsorption studies were NaF, NaCl, NaBr and NaNO_3 (Baker, Analyzed; Reagent Grade).

All solutions were prepared with distilled-deionized water. Oxygen was removed by bubbling pre-purified nitrogen through the solutions before transfer to the spectroelectrochemical cell.

Procedure

The platinum film electrodes were rinsed with water and methanol and subjected to an Argon plasma (Harrick Plasma Cleaner) for ca. 2 min to remove adsorbed organics. The platinum OTE was fitted into the lucite frame and the cell filled with a mercurous ion solution. The Hg-Pt OTE was prepared by electrochemical deposition of a ca. 50 Å thick mercury film according to a previously reported procedure [13, 14]. The cell was emptied, rinsed thoroughly with water and refilled with a degassed solution of NaF, NaCl, NaBr or NaNO_3 . A cyclic voltammogram was run to establish the potential "window" within which no faradaic current was observable. A potential step of -750 mV to potentials more positive was programmed on the PAR 175. The transmittance-time data were collected by the signal averager. Each potential modulation experiment required ca. 130 ms and was repeated 1024 times. All data was normalized to the transmittance change for one potential step.

RESULTS

The experimental results were obtained by passing 525-nm light perpendicularly through a Hg-Pt OTE and monitoring the change in transmittance which accompanied a double potential step experiment. The experiment was performed on a series of solutions containing NaF, NaCl, NaBr or NaNO₃. The potential was stepped from a negative value where no specific adsorption of these anions has been reported on mercury to more positive values at which some degree of specific adsorption occurs [17].

Figure 1 illustrates the changes in transmittance which occur for 0.1 mol l⁻¹ solutions of F⁻, Cl⁻, Br⁻ or NO₃⁻ during a potential step experiment from -750 mV to -350 mV and back to -750 mV vs. SCE. The transmittance increases when the potential is stepped in the positive direction, causing the anion to adsorb, and returns to the original value when the anion is desorbed by returning the potential to -750 mV.

Figure 2 illustrates the potential-dependence of the optical signal. The

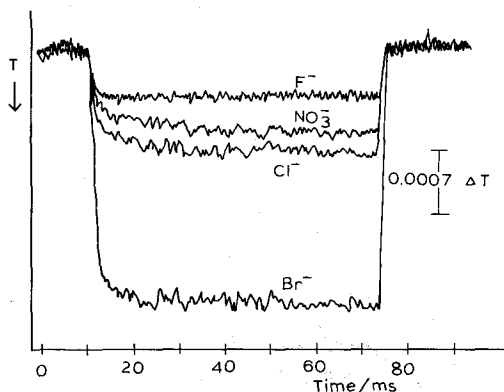


Fig. 1. Transmittance versus time behavior of 0.1 mol l⁻¹ solutions of the anion with 525-nm light. Initial potential was set at -750 mV and stepped to -350 mV. The potential was then stepped back to -750 mV.

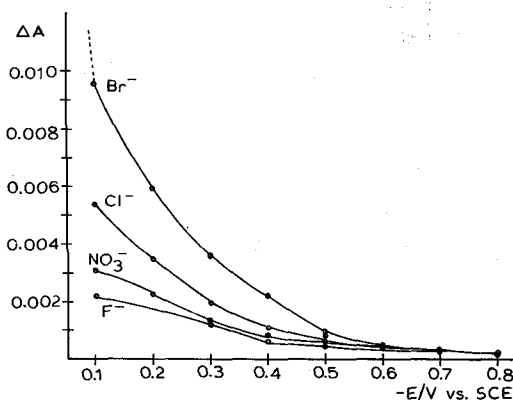


Fig. 2. Dependence of absorbance change on electrode potential for 0.1 mol l⁻¹ solutions of the anion. Each point represents 1024 signal averaged double potential step experiments from -750 mV vs. SCE to the potential indicated on the abscissa.

change in absorbance is plotted for potential steps from -750 mV to a series of more positive potentials as indicated on the abscissa. For each anion the magnitude of the optical change increases as the potential is stepped to more positive values.

DISCUSSION

The increase in transmittance which accompanies the potential step is attributed to specific adsorption of the anion in solution. The following discussion of the two figures substantiates this interpretation.

The extent of specific adsorption of anions on mercury is known to decrease in the order $\text{Br}^- > \text{Cl}^- \sim \text{NO}_3^- > \text{F}^-$. These results have been obtained by electrocapillary and differential capacitance measurements on pure mercury electrodes [17]. As shown in Fig. 1, the magnitude of the transmittance change is in the order $\text{Br}^- > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$. This result would be expected assuming that the optical signal is proportional to the amount of specifically adsorbed anion.

Figure 2 demonstrates the potential dependence of the optical signal. At large negative potentials, where the extent of adsorption is small, very little change is observed in the optical response. As the potential is stepped to more positive values the amount of specific adsorption on mercury increases as does the absorbance change. This is the same qualitative behavior which is observed when charge-potential plots are constructed from data obtained by electrocapillary measurements on pure mercury electrodes [17]. A large optical change observed at potentials more positive than about -100 mV on the Br^- data is due to the formation of a mercurous bromide film on the electrode. From cyclic voltammetry the onset of Hg_2Br_2 formation begins at about -100 mV on the Hg-Pt OTE. Identical behavior is observed for chloride, but at a more positive electrode potential.

It is interesting to note that a small signal is observed for the fluoride ion which is thought not to specifically adsorb on mercury. Some authors have postulated the specific adsorption of fluoride at positive electrode potentials [18]. Another possibility which has not been discussed in this note is that at least part of the observed signal might be due to other factors such as electrode-modulation as described by Hansen and Probst [19]. In any event, the signal is smaller than the signal obtained for the other anions and will be considered in more detail in a later paper.

ACKNOWLEDGEMENTS

The authors acknowledge support of this research by National Science Foundation Grants CHE 74-02641 and CHE 77-04399. JFG gratefully acknowledges the support of the University Research Council and the Laws' Foundation.

REFERENCES

- 1 Ying-Chech Chiu and M.A. Genshaw, *Symp. on Interfacial Phenomena, J. Phys. Chem.*, **73** (1969) 3571.
- 2 Woon-Kie Paik, M.A. Genshaw and J. O'M. Bockris, *J. Phys. Chem.*, **74** (1970) 4266.
- 3 M. Stedman, *Symp. Faraday Soc.*, **4** (1970) 64.
- 4 W.N. Hansen, *Symp. Faraday Soc.*, **4** (1970) 27.
- 5 J.D.E. McIntyre in R.H. Muller (Ed.), *Advances in Electrochemistry and Electrochemical Engineering*. Wiley-Interscience, New York, Vol. 9, 1973.
- 6 B.D. Cahan, J. Horkans, and E. Yeager, *Symp. Faraday Soc.*, **4** (1970) 36.
- 7 R.M. Lazorenko-Manevich, E.B. Brick, and Y.M. Kolotyrlin, *Electrochim. Acta.*, **22** (1977) 151.
- 8 W.N. Hansen, T. Kuwana, and R.A. Osteryoung, *Anal. Chem.*, **38** (1966) 1810.
- 9 H.B. Mark, Jr., and E.N. Randall, *Symp. Faraday Soc.*, **4** (1970) 157.
- 10 R.P. Van Duyne and D.L. Jeanmaire, *J. Electroanal. Chem.*, **84** (1977) 1.
- 11 A.J. McQuillan, P.J. Hendra, and M. Fleischman, *J. Electroanal. Chem.*, **65** (1975) 933.
- 12 A.J. McQuillan, P.J. Hendra, R.L. Paul, and M. Fleischman, *J. Electroanal. Chem.*, **66** (1975) 248.
- 13 W.R. Heineman and T. Kuwana, *Anal. Chem.*, **43** (1971) 1075.
- 14 W.R. Heineman and T. Kuwana, *Anal. Chem.*, **44** (1972) 1972.
- 15 T.P. DeAngelis, R.W. Hurst, A.M. Yacynych, H.B. Mark, Jr., W.R. Heineman, and J.S. Mattson, *Anal. Chem.*, **49** (1977) 1395.
- 16 W. von Benken and T. Kuwana, *Anal. Chem.*, **42** (1970) 1114.
- 17 P. Delahay, *Double Layer and Electrode Kinetics*. Interscience, New York, 1965.
- 18 D.J. Schiffrin, *Trans. Faraday Soc.*, **67** (1971) 3318.
- 19 W.N. Hansen and A. Prostak, *Phys. Rev.*, **174** (1968) 500.