

17. VOLTAMMETRIC INVESTIGATIONS OF NATURAL ORGANIC MATTER

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INTRODUCTION

Redox activity is one of the most important, and yet poorly understood, properties of natural organic matter (NOM). It is well known that NOM can act as a reducing agent (reductant), and this is central to the role that NOM plays in the biogeochemical cycling of carbon. More recently, there has been growing interest in the role that NOM plays as an electron shuttle (mediator) in biogeochemical cycles. For example, several recent studies have shown that the addition of NOM to cultures of iron reducing bacteria can increase the rate of dissimilatory iron reduction [1]. These effects have been attributed to polyphenolic (especially hydroquinonoid) moieties that comprise a portion of NOM [2]. There are, however, other moieties that may contribute to the overall redox activity of NOM (e.g., complexed metals [3]), and this complexity has been one of the main impediments to the development of chemically exact descriptions of redox processes involving NOM.

In our recent work in this area, we have applied electrochemical methods to the direct characterization of NOM, fractions of NOM, and model compounds for NOM or other putative electron shuttles. First, we identified a set of experimental conditions where many samples of NOM give cyclic voltammograms (CVs) that are sufficiently well-defined to allow determination of peak potentials, peak currents, etc. [4]. Now we have begun to explore electrochemical characteristics of NOM that were previously inaccessible, such as the number, potential, and reversibility of specific redox couples [5]. Part of this process involves clarifying the relationship between key experimental variables and the electrode response that they produce. Toward this end, we provide here an analysis of how previously reported voltammetric results relate to those obtained using our published method and new variations of our method that offer the possibility of further improvements in electrochemical response for NOM.

MATERIALS AND METHODS

Table 1 summarizes the materials and conditions used in this and previously published attempts to use voltammetric methods to characterize the redox properties of NOM. The main characteristics of our current method include Pt working and counter electrodes, dimethyl sulfoxide (DMSO) as the solvent, 1.0 mM NaClO₄ as the electrolyte, and a Ag/Ag⁺ reference electrode (all of our potentials are reported versus this reference). In this study, we compare the response obtained with a platinum disc working electrode (1.6 mm dia.) and a platinum microelectrode (125 μm dia.) prepared by a procedure adapted from [6].

The NOM, and fractions of NOM, we have used in this work were obtained from B. Gu (Oak Ridge National Laboratory). He obtained the raw concentrate (NOM-GT) by reverse osmosis using brown water from a wetland pond in Georgetown, SC. A fraction of NOM-GT that is enriched in polyphenolic material (NOM-PP) was obtained by elution on a column of cross-linked polyvinyl pyrrolidone polymer. NOM-PP and other fractions of NOM-GT have been characterized by UV/Vis, IR, NMR, and EPR spectroscopy [7]. For our work, stock solutions of NOM were prepared by dissolving the freeze-dried materials directly into DMSO.

Table 1. Electrochemical parameters used in voltammetric studies of NOM.

<i>Properties</i>	<i>Helburn, 1994</i>	<i>Motheo, 2000</i>	<i>Nurmi, 2002</i>	<i>New Data</i>
Working electrode	Au Wire	Ti/Ir _n Ti _n O ₂	Pt disk	Pt microelectrode
Counter electrode	Au Wire	Steel	Pt disk	Pt disk
Reference electrode	SCE	SCE	Ag/Ag ⁺	Ag/Ag ⁺
Scan Rate	500 mV/s	50 mV/s	10 mV/s	1.0-100 mV/s
Solvent	H ₂ O	H ₂ O	DMSO	DMSO
Electrolyte	0.5 M KCl	0.1 M KCl	1.0 mM NaClO ₄	1.0 mM NaClO ₄
NOM conc.	3 g/L	30 mg/L	90 mg/L	90 mg/L
NOM type	Glenamoy, Ireland HA	Mogi Guacu River peat HA	NOM-PP	NOM-PP

RESULTS AND DISCUSSION

It appears that there have been many previous attempts to obtain CVs of NOM using Hg drop electrodes, but few details of these efforts have been reported because the results suggest only adsorption and not characteristic redox reactions [e.g., 8].

that are redox inactive, and that DMSO enhances the electrode response of quinones by limiting the formation of these surface species [11]. Thus, the role of the solvent can not be fully understood without considering the role of the working electrode material.

In addition to specific chemical considerations, there are electrodynamic controls on peak shape that may offer ways to improve on the resolution of peaks that we have reported previously (e.g., Fig. 1C). Three experimental variables that affect the electrodynamic of voltammetry are the scan rate, size of the working electrode, and mixing of the solution. We have investigated the latter using a rotating disk electrode (RDE), and found that high rotation rates gave CVs with steps rather than peaks, as expected in a hydrodynamic regime where mass transport effects have been removed [5]. At slow rotation rates, our RDE studies should have been susceptible to mass transport effects because they were performed at relatively slow scan rates (10 mV/s) using a working electrode of relatively large diameter (3 mm).

Recently, we have obtained complementary results with a stationary Pt microelectrode (125 μm dia.). The CVs obtained with this electrode (Fig. 1D) show steps—similar to those obtained with the RDE—when taken at 1.0 mV/s, but peaks—similar to those shown in Fig. 1C—when taken at higher scan rates. This behavior is consistent with the lower sensitivity to mass transport effects that is expected with microelectrodes. Further optimization of the conditions used with micro- working electrodes may provide improved sensitivity (due to lower background current from charging of the electrochemical double layer) for future studies of the redox properties of NOM.

In addition, the similarity between Figs. 1C and 1D provides new evidence that the peaks we have obtained with NOM-PP are reproducible and characteristic of this particular material. In addition to the differences in working electrode design and scan rate that are noted above, the two sets of data were obtained with different lots of NOM-PP. Although we noted some differences in the voltammetric behavior of the two lots of NOM-PP (not shown), the main features of their CVs are remarkably similar (cf. Figs. 1C and 1D). This suggests that the major differences we found among the CVs of 13 different samples of NOM (Supporting Information to [5]) do reflect distinct differences in electrochemical activity. In future work, we hope to relate differences detected by voltammetry to other redox properties of biogeochemical significance.

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