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SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERIZATION OF IRON(II) AND 2,4-DINITROTOLUENE

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Abstract

The objective of this work was the development of reliable methods to determine 2,4-dinitrotoluene, a precursor to explosives. A complex between Fe(II) ion and 2,4-dinitrotoluene was formed in solution and characterized by ultraviolet-visible absorption spectroscopy using Job's plots and attenuated total reflection-Fourier transform infrared spectroscopy. Surface modification of glassy carbon electrodes were performed with iron nanoparticles via electrochemical reduction of iron(II). The modified electrode was employed for the determination of 2,4-dinitrotoluene. Scanning electron micrographs showed that the iron nanoparticles were incorporated on the surface of glassy carbon electrode. The electrochemical determination of 2,4-dinitrotoluene was performed by cyclic voltammetry using the modified electrode. The iron modified electrode produced larger reduction currents than the unmodified electrode for the same concentration of 2,4-dinitrotoluene. Concentrations of 2,4-dinitrotoluene as low as 10 parts per billion were determined using the modified electrode.

Keywords

2,4-dinitrotoluene; Attenuated total reflection-Fourier transform infrared spectroscopy; Cyclic voltammetry; Surface modified electrode

INTRODUCTION

The determination of dinitrotoluenes is of interest because of significant environmental and safety concerns (Toal and Trogler 2006; Davies et al. 2008). Dinitrotoluenes have been reported in air, surface water, groundwater, and soil, as well as in furniture foam, ammunition, and dyes. Furthermore, dinitrotoluenes are used as precursors for explosives. Exposure to high concentrations may cause lung and liver complications as well as reproductive problems. Therefore, it is important to develop better analytical methods for dinitrotoluenes.

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SUPPLEMENTAL MATERIAL

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Current methods to determine dinitrotoluenes include gas chromatography (Walsh 2001), fluorescence (Goodpaster and McGuffin 2001), electrochemical methods (Wang, Hocesvar, and Ogorevc 2004; Alizadeh et al. 2010; J.-C. Chen et al. 2006; T.-W. Chen et al. 2011; Hrapovic et al. 2006; Zhang et al. 2006), Raman spectroscopy (Ko, Chang, and Tsukruk 2009), and chemiluminescence (Jimenez and Navas 2004). Electrochemical methods have been shown to possess advantages that include high selectivity, easy operation, low cost, and easy portability. To improve the performance of electrochemical analysis, the surface area of the electrodes has been increased by attaching materials to the electrodes. Single walled carbon nanotubes, multiwalled carbon nanotubes (Wang, Hocesvar, and Ogorevc 2004), and polymer/silica composites (Zhang et al. 2006) have been employed to improve electrochemical determination. Electrodes modified with carbon nanotubes have been shown to produce enhanced sensitivity due to strong hydrophobic interactions between the analytes and the carbon nanotubes (R. J. Chen et al. 2001; Liu et al. 2007).

In this work, iron based materials were employed to improve the performance of glassy carbon electrodes. Iron nanoparticles were attached to the electrode to increase the surface area by depositing iron from solution. The goal was to enhance the determination 2,4-dinitrotoluene, the most common of these compounds and a precursor to trinitrotoluene.

As the determination of 2,4-dinitrotoluene by electrochemistry involves the interaction with the surface of the electrode, the reaction between dinitrotoluenes with aqueous Fe(II) was investigated. Based on the results, iron nanoparticles were incorporated on the surface of glassy carbon electrodes with application for the electrochemical determination of dinitrotoluenes. The interaction between 2,4-dinitrotoluene and iron(II) is reported using absorption spectroscopy and Fourier transform infrared spectroscopy. The electrochemical surface modification of glassy carbon electrodes with iron nanoparticles is described, as well as the application of the modified electrode for the determination of 2,4-dinitrotoluene by cyclic voltammetry (CV).

EXPERIMENTAL

Materials

Sodium acetate, potassium chloride, and acetic acid were purchased from Sigma-Aldrich. 2,4-Dinitrotoluene and acetonitrile were obtained from Acros Organics. Iron(II) sulfate was obtained from Fischer Scientific (USA) and used as received. A 5 millimolar stock solution of Fe(II) was prepared in 0.1 molar KCl and served as the supporting electrolyte for deposition experiments. The stock solution of 2,4-dinitrotoluene at 5 millimolar in 1 molar was prepared in acetate buffer for spectroscopy experiments and a stock solution of 1 millimolar was prepared in acetonitrile and diluted to of 100, 50 and 10 parts per billion (ppb) in the 0.1 molar KCl solution for quantitative measurements.

Spectroscopy

Absorption spectroscopy—Solutions of Fe(II) ions were prepared to 5 millimolar in acetate buffer at pH 4.0. A concentration of 5 millimolar 2,4-dinitrotoluene was prepared in acetate buffer at pH 4.0. For Job's plots, various volume proportions of metal to ligand

solutions were prepared to generate a linear mole fraction ratio between the metal and ligand solutions, by increasing the concentration of metal and decreasing the concentration of ligand (Hill and MacCarthy 1986). Once the metal to ligand solutions were prepared, ultraviolet-visible spectroscopy (Cary 50, Agilent, Santa Clara, CA, USA) was used for determination at room temperature. The solutions turned orange-bronze color indicating that the metal/ligand interaction was occurring. Spectroscopically, the interaction was observed with the appearance of an absorption peak at 465 nanometers (Supplementary Figure S1). The absorption spectra of Fe(II) and 2,4-dinitrotoluene alone were recorded and used as references for these experiments.

Job's Method is characterized by a complex formation constant, K_f , which is calculated from following Equation (1):

$$K_f = \frac{A_2/A_1}{C_M \left(1 - \frac{A_2}{A_1}\right)^2} \quad (1)$$

where C_M is the initial analytical concentration of the iron at the maximum absorbance values of A_1 and A_2 . The value of A_1 value is obtained from the intersecting lines of the extrapolated linear equations and A_2 represents the maximum absorbance value.

Attenuated total reflection-fourier transform infrared spectroscopy—Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was performed with a Spectrum BX instrument (PerkinElmer, Waltham, MA, USA) equipped with a one-reflection mirror ATR mount at 4.0 per centimeter resolution from 2000 to 600 per centimeter with 128 scans every 1.0 per centimeter. The single reflection disc consisted of a ZnSe crystal at an incidence angle of 45°. After each measurement, the crystal was washed with ethanol, and allowed to air dry. For ATR-FTIR measurements, approximately 10 microliters of sample were transferred from a small tube, placed on the ZnSe crystal, and allowed to dry to produce a thin-layer film. Spectra were obtained for solutions of 2,4-dinitrotoluene in the absence and presence of Fe(II) ions. The spectra were plotted versus percent transmittance after the subtraction of the noise.

Electrochemical Measurements

Cyclic voltammetry was performed using an electrochemical analyzer CHI440A (CH Instruments, Austin, TX, USA) connected to a computer. A three-electrode system was used, consisting of a modified glassy carbon electrode or unmodified glassy carbon electrode as a working electrode (3 millimeters diameter), while Ag/AgCl and platinum wire served as the reference and counter electrodes, respectively. Electrochemical experiments were performed in a 2-milliliters voltammetric cell at room temperature. All potentials were referenced to the Ag/AgCl electrode. Scanning electron microscopy (SEM) was performed on a Jeol 6610LV ope (JEOL, Peabody, MA, USA). The SEM was coupled to an energy dispersive X-ray spectrophotometer (EDS, Quantax200, Bruker, Fitchburg, WI, USA).

A glassy carbon electrode was cleaned and polished to a mirror-like surface with water. The bare electrode was scanned in a cycle between -1.2 and $+1.2$ volt in 0.1 molar KCl to obtain

background. Cyclic voltammetry was used to deposit iron nanoparticles on the electrode surface. Iron nanoparticles were deposited by cyclic sweeping from -1.2 to $+1.2$ volts at 75 millivolts per second for 30 , 70 , and 150 cycles in 5 millimolars FeSO_4 containing 0.1 molar KCl solution. The modified electrodes were rinsed with water and air dried for further use.

The iron modified glassy carbon electrode was placed in a 0.1 molar KCl buffer containing the desired concentration of $2,4$ -dinitrotoluene. Cyclic voltammetry experiments were performed from -1.2 to 0.0 volt at 75 millivolts per second.

RESULTS AND DISCUSSION

Ultraviolet-visible Spectroscopy

Quantitative and qualitative analysis of the binding properties of $2,4$ -dinitrotoluene with Fe(II) ions were investigated in acidic solution. The spectral properties of the complex ions were also studied in the presence and absence of iron. The structural properties of iron alone were also considered when characterizing the complex. The metal to ligand ratio of the complex binding formation was determined using Job's Method of continuous variation. Infrared spectroscopy was used to qualitatively characterize the binding of $2,4$ -dinitrotoluene to iron.

Various ratios of $2,4$ -dinitrotoluene and Fe(II) were mixed and absorption spectra were recorded. In comparison with the absorption spectra of free $2,4$ -dinitrotoluene and that of free Fe(II) , there was a new peak at 460 nanometers and strong absorption up to 570 nanometers in the mixture, which suggested the formation of a complex (Supplementary Figure S2). The A_1 value, corresponding to the break point of the extrapolated line equation, was calculated to be 0.1765 . The maximum absorption, A_2 , was 0.18525 at $X_L=0.5$. The formation constant, K_f , value for the reaction was calculated to be 8.62×10^4 . The maximum absorbance value was obtained at a metal to ligand ratio of 0.5 denoting a $\text{Fe(II)}/2,4$ -dinitrotoluene charge transfer complex of $1:1$. Figure 1 shows the Job's Method plot of the complex at different metal to ligand ratios ($2,4$ -dinitrotoluene and Fe(II)).

Infrared Spectroscopy

The complex between Fe(II) and $2,4$ -dinitrotoluene was confirmed by the infrared measurements. The binding between Fe(II) and $2,4$ -dinitrotoluene showed shifting of the infrared peaks of the nitro group and the aromatic ring and new peaks from the metal-oxygen bonds. In Figure 2 and Table 1, the $\nu_{(\text{C}=\text{C})}$ of the aromatic ring of the $2,4$ -dinitrotoluene molecule occurred at approximately 1604 per centimeter (Stewart, Bosco, and Carper 1986). Once the $2,4$ -dinitrotoluene formed a complex with the Fe(II) ion, the corresponding peak shifted to approximately 1637 per centimeter. The difference between the unbound $2,4$ -dinitrotoluene $\text{C}=\text{C}$ bond in the aromatic ring to the bound $2,4$ -dinitrotoluene in the ligand-complex $\text{C}=\text{C}$ aromatic ring bond was 33 per centimeter. The nitro peaks occurred at 1345 and 1529 per centimeter in free $2,4$ -dinitrotoluene (Stewart, Bosco, and Carper 1986). In the metal-ligand complex, the nitro peaks shifted to 1407 and 1558 per centimeter, respectively. Nitro groups have been reported to bond to metal centers (Driessen, van Geldrop, and Groeneveld 1970). The peaks were broadened after complex

formation due to the interaction between Fe(II) and 2,4-dinitrotoluene. When the metal-ligand complex was formed, the electron density of the aromatic ring was perturbed by the donation of electrons from the ligand to the iron, which resulted in reduced electron density in the aromatic ring and shifted the corresponding peaks. There were also peaks from iron-oxygen bonding at 1020, 792, and 643 per centimeter (White and Roy 1964). These changes indicated strong interaction of the 2,4-dinitrotoluene with Fe(II), confirming the ultraviolet-visible spectroscopy results.

Scanning Electron Microscopy

A scanning electron micrograph of iron nanoparticles on glassy carbon is shown in Figure 3, demonstrating that iron was densely dispersed on the surface. Many of the particles were less than a micrometer in size and some were as small as 200 nanometers. There appeared to be an aggregation of the nanoparticles to form larger particles in some areas of the electrode. Figure 4 shows the mapping of the modified surface, displaying the presence of well-dispersed iron on the surface.

Electrochemistry

Cyclic voltammograms of 2,4-dinitrotoluene show a reduction around -0.9 volt. Figure 5 compares cyclic voltammograms of 10 parts per billion 2,4-dinitrotoluene on the unmodified and iron modified glassy carbon electrodes. The cyclic voltammograms show that the modified electrodes produced higher reduction peak currents than the unmodified electrode. The reduction current increased as the number of deposition scans increased. Figure 5 shows a significant increase in the peak current and a negative shift of the peak potential as the number of scans increased. Figures 6 and 7 show similar behavior for 50 and 100 parts per billion 2,4-dinitrotoluene, respectively. A concentration of 10 parts per billion of 2,4-dinitrotoluene was detectable in this study, which is inferior to the value reported by Zang et al. (2011). However, this result is superior to other literature reports (T.-W. Chen et al. 2011; Fierke et al. 2012).

The peak at -0.9 volt may be attributed to the electrochemical reduction of 2,4-dinitrotoluene and has been described previously (Chua and Pumera 2011; Zhang et al. 2011; Fierke et al. 2012; Caygill et al. 2013; Wang et al. 2014). The reduction occurs via two reaction steps: a four-electron reduction of the nitro group produces a hydroxylamine group, followed by conversion to an amine group.

The increase in reduction peak current with the number of deposition scans indicates that the iron nanoparticles may facilitate adsorption of 2,4-dinitrotoluene from solution to the electrode by increasing the surface area of the modified electrode. The strong increase in the reduction peak current on the modified glassy carbon electrode shows the potential of iron nanomaterials in improving the sensitivity for the determination of nitroaromatic explosives.

Figures 5, 6, and 7 show two reductions observed with the unmodified electrode at -0.55 and -0.9 volt that were assigned to the reductions of the 4- and 2-nitro groups, respectively (Toh, Ambrosi, and Pumera 2013). In contrast, there was no reduction peak at -0.55 volt with the modified electrode. However, the reduction peaks overlapped at -0.9 volt, producing a broad peak. These phenomena were also observed in the oxidation of 2,4-

dinitrotoluene. In Figure 5, two oxidation peaks were located at -0.6 and -1.1 volts for the unmodified electrode. However, there was only one broad peak at -0.6 volt for the modified electrode. The explanation is that 2- and 4-nitro groups in 2,4-dinitrotoluene experience similar electrochemical conditions because of interaction through 2- and 4-nitro groups with iron (II). This explanation is in agreement with the infrared spectra. A reduction at -0.9 volt was also observed with the bare electrode in the absence of iron, and, therefore, this reduction cannot be assigned to the reduction of the metal.

CONCLUSIONS

Iron(II) ions produce complexes with 2,4-dinitrotoluene in aqueous solution at low pH that were characterized by ultraviolet-visible absorption spectroscopy with Job's plots and infrared spectroscopy. Glassy carbon electrodes were modified by electrochemical reduction of Fe(II) for use in the electrochemical determination of 2,4-dinitrotoluene. Scanning electron microscopy confirmed the deposition of the iron nanoparticles and energy dispersive X-ray spectroscopy showed that the iron was well dispersed on the surface. Cyclic voltammetry showed that the modified electrode produced higher currents compared to unmodified electrodes. The reduction current increased with the number of deposition scans. These results show that the deposited iron nanoparticles significantly changed the surface of the electrode due to the enhanced current of 2,4-dinitrotoluene. These results show the potential of the modified glassy carbon electrode for the determination of aromatic nitroexplosives. Iron nanomaterials may be a practical alternative electrode material for electrochemical analysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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REFERENCES

- Alizadeh T, Zare M, Ganjali MR, Norouzi P, Tavana B. A new molecularly imprinted polymer (MIP)-based electrochemical sensor for monitoring 2,4,6-trinitrotoluene (TNT) in natural waters and soil samples. *Biosensors and Bioelectronics*. 2010; 25:1166–1172. [PubMed: 19892541]
- Caygill JS, Collyer SD, Holmes JL, Davis F, Higson SPJ. Disposable screen-printed sensors for the electrochemical detection of TNT and DNT. *The Analyst*. 2013; 138:346–352. [PubMed: 23152954]
- Chen J-C, Shih J-L, Liu C-H, Kuo M-Y, Zen J-M. Disposable electrochemical sensor for determination of nitroaromatic compounds by a single-run approach. *Analytical Chemistry*. 2006; 78:3752–3757. [PubMed: 16737233]
- Chen RJ, Zhang Y, Wang D, Dai H. Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization. *Journal of the American Chemical Society*. 2001; 123:3838–3839. [PubMed: 11457124]

- Chen T-W, Sheng Z-H, Wang K, Wang F-B, Xia X-H. Determination of explosives using electrochemically reduced graphene. *Chemistry - An Asian Journal*. 2011; 6:1210–1216.
- Chua CK, Pumera M. Influence of methyl substituent position on redox properties of nitroaromatics related to 2,4,6-trinitrotoluene. *Electroanalysis*. 2011; 23:2350–2356.
- Davies AG, Burnett AD, Fan W, Linfield EH, Cunningham JE. Terahertz spectroscopy of explosives and drugs. *Materials Today*. 2008; 11:18–26.
- Driessen WL, van Geldrop LM, Groeneveld WL. Complexes with ligands containing the nitro group: Part III. Metal(II) nitrobenzene solvates. *Recueil des Travaux Chimiques des Pays-Bas*. 1970; 89:1271–1275.
- Fierke MA, Olson EJ, Buhlmann P, Stein A. Receptor-based detection of 2,4-dinitrotoluene using modified three-dimensionally ordered macroporous carbon electrodes. *ACS Applied Materials & Interfaces*. 2012; 4:4731–4739. [PubMed: 22905948]
- Goodpaster JV, McGuffin VL. Fluorescence quenching as an indirect detection method for nitrated explosives. *Analytical Chemistry*. 2001; 73:2004–2011. [PubMed: 11354482]
- Hill ZD, MacCarthy P. Novel approach to Job's method: An undergraduate experiment. *Journal of Chemical Education*. 1986; 63:162.
- Hrapovic S, Majid E, Liu Y, Male K, Luong JHT. Metallic nanoparticle– carbon nanotube composites for electrochemical determination of explosive nitroaromatic compounds. *Analytical Chemistry*. 2006; 78:5504–5512. [PubMed: 16878889]
- Jimenez AM, Navas MJ. Chemiluminescence detection systems for the analysis of explosives. *Journal of Hazardous Materials*. 2004; 106:1–8. [PubMed: 14693433]
- Ko H, Chang S, Tsukruk VV. Porous substrates for label-free molecular level detection of nonresonant organic molecules. *ACS Nano*. 2009; 3:181–182. [PubMed: 19206265]
- Liu Z, Sun X, Nakayama-Ratchford N, Dai H. Supramolecular chemistry on water-soluble carbon nanotubes for drug loading and delivery. *ACS Nano*. 2007; 1:50–56. [PubMed: 19203129]
- Stewart JJP, Bosco SR, Carper WR. Vibrational spectra of 2,4,6-trinitrotoluene and its isotopically substituted analogues. *Spectrochimica Acta Part A: Molecular Spectroscopy*. 1986; 42:13–21.
- Toal SJ, Trogler WC. Polymer sensors for nitroaromatic explosives detection. *Journal of Materials Chemistry*. 2006; 16:2871–2883.
- Toh HS, Ambrosi A, Pumera M. Electrocatalytic effect of ZnO nanoparticles on reduction of nitroaromatic compounds. *Catalysis Science & Technology*. 2013; 3:123–127.
- Walsh M. Determination of nitroaromatic, nitramine, and nitrate ester explosives in soil by gas chromatography and an electron capture detector. *Talanta*. 2001; 54:427–438. [PubMed: 18968268]
- Wang J, Hocevar SB, Ogorevc B. Carbon nanotube-modified glassy carbon electrode for adsorptive stripping voltammetric detection of ultratrace levels of 2,4,6-trinitrotoluene. *Electrochemistry Communications*. 2004; 6:176–179.
- Wang J, Jin W, Zhang X, Hu C, Luo Q, Lin Y, Hu S. Rapid in situ detection of ultratrace 2,4-dinitrotoluene solids by a sandwiched paper-like electrochemical sensor. *Analytical Chemistry*. 2014; 86:8383–8390. [PubMed: 25072393]
- White WB, Roy R. Infrared spectra-crystal structure correlations: II. Comparison of simple polymorphic minerals. *The American Mineralogist*. 1964; 49:1670–1687.
- Zang J, Guo CX, Hu F, Yu L, Li CM. Electrochemical detection of ultratrace nitroaromatic explosives using ordered mesoporous carbon. *Analytica Chimica Acta*. 2011; 683:187–191. [PubMed: 21167969]
- Zhang H-X, Cao A-M, Hu J-S, Wan L-J, Lee S-T. Electrochemical sensor for detecting ultratrace nitroaromatic compounds using mesoporous SiO₂-modified electrode. *Analytical Chemistry*. 2006; 78:1967–1971. [PubMed: 16536434]

Figure 1. Stoichiometry of the 2,4-dinitrotoluene–Fe(II) complex by Job's method at 465 nanometers, Initial concentrations of 2,4-dinitrotoluene and iron(II) solutions: 5 millimolars at pH 4.0 and 25 degree Celsius.

Figure 2.
Attenuated total reflection infrared spectra of (a) 5 millimolars 2,4-dinitrotoluene and (b) 2,4-dinitrotoluene in Fe(II) in acetate buffer at pH 4.0.

Figure 3.
Scanning electron micrograph of the modified iron nanoparticle glassy carbon electrode.

Figure 4.
Energy dispersive X-ray spectrum of the modified iron nanoparticle glassy carbon electrode.
Iron is indicated by red.

Figure 5. Cyclic voltammograms of 10 parts per billion of 2,4-dinitrotoluene: (a) 150 scans with the electrode modified with iron nanoparticles, (b) seventy scans with the modified electrode, (c) thirty scans with the modified electrode, and (d) thirty scans with the unmodified electrode.

Figure 6.

Cyclic voltammetric curves of 50 parts per billion of 2,4-dinitrotoluene: (a) 150 scans with the modified electrode with iron nanoparticles, (b) seventy scans with the modified electrode, (c) thirty scans with the modified electrode, and (d) thirty scans with the unmodified electrode.

Figure 7.

Cyclic voltammetric curves of 100 parts per billion of 2,4-dinitrotoluene: (a) 150 scans with the modified electrode with iron nanoparticles, (b) seventy scans with the modified electrode, (c) thirty scans with the modified electrode, and (d) thirty scans with the unmodified electrode.

Table 1

Infrared assignments for 2,4-dinitrotoluene and the Fe(II)–2,4-dinitrotoluene complex

Wavenumber (per centimeter)		
2,4-Dinitrotoluene	Complex	Assignment
1604	1637	C-C ring stretch
1529	1558	NO ₂ asymmetric stretch
1345	1407	NO ₂ symmetric stretch
1205		Ring H-C-C in-plane bending
1151		Ring H-C-C in-plane bending
1067		C-H out-of-plane bending of ring
917		C-H out-of-plane bending of ring
835		CH ₃ rocking
791		C-N bending
732		C-N-O bending
705		C-N-O bending
	1020, 792, 643	Fe-O