

Original article

Voltammetric determination of stability constants of lead complexes with diallyl disulfide, dimethyl disulfide, and diallyl sulfide



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ABSTRACT

The complexation of Pb²⁺ by diallyl disulfide (DADS), dimethyl disulfide (DMDS) and diallyl sulfide (DAS) has been studied by differential pulse voltammetry. Stability constants, (log β), of the 1:1 (PbL) and 1:2 (PbL₂) complexes, where L = ligand, were found to be in the range of ca. 3.8–4.2 and 9.4–10.2, respectively. Complex formation is accompanied with a significant decrease in the peak current and the shift of the Pb²⁺/Pb half-wave potential to a higher one upon the addition of the sulfur containing ligands (L). The formation of 1:1 and 1:2 complexes, i.e., PbL²⁺ and PbL₂²⁺ was observed in the case of the three ligands. The consecutive formation constants of labile lead complexes with DADS, DMDS, and DAS were determined at 298 K by the method of DeFord and Hume. Apparently due to the large size of the lead ion, steric hindrance caused by the greater steric bulk of DADS compared to that of DMDS have little or no effects on the formation constants, so that very similar values were obtained in the case of the two ligands. Also, the possible participation of C=C double bonds in coordination with the metal center in the case of DADS appears to compensate for the steric effects caused by the larger size of this ligand. In agreement with the Jorgensen principle of symbiosis, the second formation constants were found to be approximately six orders of magnitude greater than the first ones.

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1. Introduction

Lead is a highly toxic metal found in the Earth's crust. Because of its abundance, low-cost, and physical properties, lead and lead compounds were used in a wide variety of products including paint, ceramics, pipes, solders, gasoline, batteries, and cosmetics. Lead is a serious cumulative body poison and enters our body system through food, water, and air [1], since Pb²⁺ inhibits –SH enzymes, especially by interaction with cysteine residues in proteins [2]. Although the total human exposure to lead has been significantly reduced due to the controls on lead in gasoline and on industrial air emissions, lead poisoning is still a serious public health problem [3,4]. Drinking water is another possible source of lead exposure [5–7] and other main sources of lead exposure are lead-based paints and lead-contaminated dusts or soils [8], plumbing materials and equipment, car batteries, lubricating compounds and foods prepared in lead-glazed ceramics [4]. The

human body is only able to excrete lead very slowly, consequently, it can accumulate in the bones and liver where it reacts with cell membranes to alter their permeability, or destroys them completely [9]. Chronic lead poisoning can impair memory and cause headaches, abdominal pain, anemia, aggressive behavior, and learning disabilities. In fact, health experts claim that lead poisoning is an entirely preventable environmental health disease in children [10].

Chemopreventive agents have been used against the toxic effect of many compounds, including heavy metals. A range of vegetables, plants and synthetic compounds have been screened in order to ascertain whether they have potential in the prevention and cure of many diseases and conditions [12]. As one plant studied extensively, garlic (*Allium sativum*), has been used since ancient times as a cure for many diseases [13]. It has antifungal, antithrombotic, antibacterial, antihypertensive, anti-carcinogenic, and antioxidant properties [14].

Garlic belongs to the family *Liliaceae* and has a higher concentration of sulfur compounds which yield the characteristic flavor and taste and are also responsible for the beneficial effects [15]. In this respect, garlic aids the liver in lowering the levels of heavy metal especially lead, cadmium and mercury [11]. When

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garlic is minced, or crushed, the allyl sulfur compounds are formed by enzymatic activity. These extracts are composed of allicin, water-soluble *S*-allylmercaptocysteine and *S*-allylcysteine, and oil-soluble diallyl disulfide (DADS), diallyltrisulfide and diallyl sulfide [16,17], and additionally, allicin also consists of DADS, diallyl sulfide (DAS), diallyltrisulfide (DTS) and sulfur dioxide [18]. Organosulfur compounds can adsorb on the surface of gold or silver electrodes through several chemisorption steps. Thiols and disulfides compounds can adsorb by an anodic oxidation process on the surface of Au and Ag [19]. The study of the binding of lead (II) to the organic sulfur compounds of garlic oil and extracts is especially of importance in the modeling of the inhibitory effects of garlic on the lead poisoning. In the Pearson hard and soft acid and base sense, lead ions are classified as soft and, hence, should form complexes with sulfur containing ligands due to the soft character of the sulfur atom [18,20]. Of note, the compound 2,3-dimercaptopropanol (SHCH₂CH(SH)CH₂OH), also known as British anti-Lewisite, is a strong chelating agent which has been used in the treatment of lead poisoning [2].

Complexation of Pb²⁺ with various ligands, such as vitamin C [21], 2,5-dimercapto-1,3,4-thiadiazole [22], dicyclohexano-18-crown-6 [23], and glutathione [24], has been investigated. Voltammetric techniques are widely used to study the interactions between metal ions and various ligands [25] because of their very high reproducibility and reliability at low concentrations [26] and also due to their ability to detect different chemical forms of the same element [21]. The usual strategy with the use of voltammetric modeling involves: first, the assumption of the physico-chemical phenomena taking place during the measurements, and secondly, the use of fundamental equations (Nernst equation, Fick laws of diffusion, equilibrium constants, kinetic equations, etc.) to generate a set of equations which can be analytically or numerically solved [27]. As a result, to obtain quantitative information is through the postulation of an electrochemical model and its mathematical solution followed by the fitting of the parameters of the equations of the model to the experimental data [28].

In this study, the cumulative stability constants (β) of three organic sulfur compounds, DADS, DMDS and DAS (Fig. 1), which are compounds of garlic oil [29] that complex with Pb²⁺ have been measured using differential pulse voltammetry (DPV) and a gold electrode. The information about metal complexation is provided from the fitting of the parameters of the model to the experimental data.

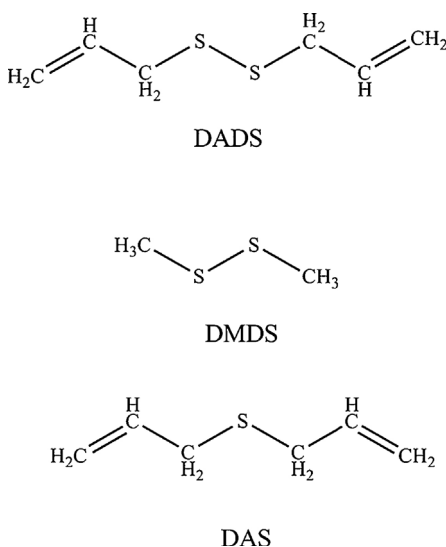


Fig. 1. Organic sulfur compounds used in this study.

2. Experimental

2.1. Chemicals and instrumentation

Diallyl disulfide, dimethyl disulfide and diallyl sulfide, lead nitrate, sulfuric acid, acetic acid, sodium hydroxide, and boric acid were purchased from Merck or Sigma–Aldrich analytical grade. A stock solution of the ligands (0.01 mol/L of DADS, DMDS, and DAS) was prepared by dissolving appropriate amounts of each in 40 mL distilled methanol and diluting to volume in a 100 mL calibrated flask with distilled water. Stock lead ion solution (0.02 mol/L) was prepared by dissolving an appropriate amount of Pb(NO₃)₂ in doubly distilled water.

Electrochemical experiments (differential pulse voltammetry, DPV) were carried out using a Computrace 757 VA from Metrohm. In all cases, a three-electrode system consisting of a gold electrode as the working electrode with the diameter of two mm from Metrohm, a platinum wire counter electrode and an Ag/AgCl, KCl (3 mol/L) reference electrode was used. All electro-chemical measurements were carried out in a 12 mL cell.

The gold electrode was abraded with a fine grade of furriery paper and polished to a mirror-like surface with 0.05 mm Al₂O₃ powder, and immersed in NaOH (0.2 mol/L) then rinsed ultrasonically with water and ethanol for 3 min.

2.2. Voltammetric measurements

Electrochemical measurements were performed in the solutions of acetate buffer pH 5.5, with ionic strength 0.10 mol/L. All the measurements were carried out in a glass cell at r.t. (25 °C) and the solutions were purged with nitrogen for at least 30 min prior to each experiment and the nitrogen atmosphere was maintained thereafter and DPV for each addition was recorded at a sweep rate of 0.1 V/s. The starting and ending potentials of all the titration experiments were from 0.2 to –0.6 V vs. Ag/AgCl. After recording each voltammogram (at different ligand to metal molar ratios), the electrode surface was cleaned electrochemically by applying the potential of 1.5 V for 100 s. Each titration experiment was repeated at least four times. The voltammograms were smoothed and converted into data matrices by means of internally written programs implemented in MATLAB.

3. Results and discussion

3.1. Optimization of conditions

The electrochemical study of the complexation of thiol-containing ligands with lead ion is faced with difficulties caused by the high affinity of thiol-containing ligands, or their complexes, onto the surface of electrode. In the present study, the complex formation between Pb²⁺ and DADS, DMDS and DAS has been studied by DPV. A simple voltammetric method was proposed for *in situ* and simultaneous cleaning of the electrode surface. According to the results, applying a high positive potential (+1.5 V for 100 s) can remove the organic sulfur compounds of garlic oil and their complexes from the surface of electrode after each voltammogram.

The complexation of Pb²⁺ with the subject ligands in aqueous solution can be affected by a variety of factors and conditions, such as the type of electrode, type of buffer solution, pH and initial concentration of metal ions, all of which were considered in this study. Although electrodes, such as mercury film, glassy carbon, carbon paste and platinum electrode, were also checked for this purpose, it was experimentally verified that the changes in the voltammograms during the titration were not enough for the evaluation of the stability constants, and therefore a gold disk

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