♻EPA ENVIRONMENTAL RESEARCH BRIEF

Lanthanide Ion Probe Spectroscopy for Metal Ion Speciation

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Abstract
A unique process model that intimately involves the experimental and mathematical aspects of metal-organic interactions was developed. The technique, LIPSMIS (Lanthanide Ion Probe Spectroscopy for Metal Ion Speciation), in its present form, provides for experimental verification of predictions of the quantitative values derived from modeling organic interactions. Although it is cast in its present form to treat binding of metal ions by humic substances, LIPSMIS is sufficiently general that it can be modified to model metal ion binding with inorganic anions or with sites on organic substances other than humics.

Introduction
Research in metal-organic interactions at the Environmental Research Laboratory, Athens, Georgia has the prime objective of providing the necessary scientific knowledge with which to build decision-making tools for EPA's regulatory offices. For example, implementation of both the Hazardous and Solid Waste and Superfund Acts requires tools for evaluation of alternative waste management and treatment technologies, based on potential human health and environmental impacts. These tools include exposure assessment models for estimating the fate and transport of toxic metals to either an environmental or human receptor. Currently, the prime model for this purpose is MINTEQA2, a thermodynamic equilibrium model for prediction of metal speciation, and thus of metal mobility.

Dissolved organic material (DOM), e.g., humic substances, are an important component of most surface waters and soil systems, and even occur to a significant extent in some aquifer solids. Toxic chemicals, such as metals, may bind with DOM, leading to mobilization if the DOM is in a dissolved ôr colloidal state. MINTEQA2 does not contain a term representing the interactions of metals with naturally occurring organic materials.

The long range goal of our research is to develop a quantitative term (a mathematical process model) to describe metal-natural organic binding. However, before this is possible, it is necessary to develop techniques to experimentally measure the strength and extent of metal-organic interactions under the influence of environmental variables such as pH, ionic strength, and metal ion competition for the various binding sites of the DOM without severely perturbing the state of the system as these measurements are made.

Experimental
The LIPSMIS technique is based on the unique fluorescence properties of the trivalent europium ion, Eu(III). The basis of this technique is the existence of a hypersensitive transition associated with the fluorescence emission spectrum of the Eu(III) ion. The intensity of the ~616nm emission band of the Eu(III) ion is extremely sensitive to ligation, whereas the intensity of the ~592 nm emission band is not. This results in an increase in the intensity of the 616 band relative to the 592 band as the Eu(III) metal ion is bound to a ligand site, for example, a carboxylic site on a humic material. This intensity ratio (Ratio = I_{592}/I_{616}) can then be quantitatively related to the concentrations of the free and bound metal species. Therefore, the change in this ratio as a function of total metal added is essentially a spectroscopic titration of the metal binding sites of the humic (other) material present.

Two experimental problems had to be addressed, however, before this type of measurement could be deemed viable.

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First, the cross section for spectroscopic absorption for the Eu(III) ion is vanishingly small (~10au as compared to 10000 for most organics). This was solved by exciting the Eu(III) emission with a high peak power, low average power pulsed dye laser operating at the Eu(III) absorption line at ~394nm. Second, at this wavelength the humic material fluoresced with very high efficiency. The humic emission could be up to 10^6 times as strong as the Eu(III) signal at low Eu(III) concentrations. To overcome this large mismatch, the spectral properties of Eu(III) were used to separate the signals. The fluorescence lifetimes of most organics are in the nanosecond range, whereas the lifetime of the nearly forbidden Eu(III) transitions are in the millisecond range. By using a combination of phototube pulsing and signal time gating, the Eu(III) fluorescence signal could be easily extracted from the extremely intense humic emission. Details of the experimental setup are discussed by Dobbs and coworkers[1].

A Model for Metal-Organic Binding

The present metal-organic interaction model is based on the continuous distribution model used for proton binding[1] with humic substances. This distribution is characterized by three descriptor variables: C_L, the total concentration of metal or proton binding sites, μ, the mean Log K_i value and σ, the breadth of the distribution of K_i values. K_i is the cation - organic binding constant, a measure of binding strength.

The effect of competitive binding was incorporated into the model by using a form of the competitive Langmuir equation such that all cations (hydrogen ions and metal cations) compete for the same distribution of ligand binding sites[2]. The effect of ionic strength of the aqueous medium on binding was found to be easily modeled by expressing the activities of all species in equilibrium. The simple Davies model was found to be satisfactory for calculating activity coefficients.

Although the binding of Eu(III) to humic materials is not of particular environmental interest, it can be used as a sensitive probe for measuring effects of pH and ionic strength on metal binding. When a second metal, e.g., a

toxic environmental pollutant, is added, the competition for sites between Eu(III) and this metal can be monitored as a displacement of Eu(III) and concomitant increase in the measured fluorescence intensity ratio

Effect of pH

Figure 1 shows the effect of pH on metal binding with Suwannee River fulvic substances. The symbols are experimentally observed values and the solid lines are calculated from the metal organic interaction model

The effects of pH are most pronounced in pH ranges below 5. As the pH is decreased, the probe metal is released from the humic substance, and the fluorescence ratio increases. The complexation capacity of the humic material is a strong function of the pH of the aqueous medium

Effect of Ionic Strength

Figures 2 and 3 show the effect of ionic strength on metal binding with Suwannee River dissolved organic matter (SRDOM) at pH 3.5 and pH 6 2

In both cases an increase in ionic strength results in a release of metal ion and an increase in the fluorescence ratio. The effect is most pronounced at lower pH.

Effect of metal competition

Figure 4 shows the effect of Pb(II) ions competing with the europium probe ion for humic binding sites.

The symbols represent observed values and the solid lines are calculated from the model. The competitive binding model developed here allows the LIPSMIS technique to serve as a general tool for measuring the binding strength of any metal that competes with the probe metal for binding sites on the humic material.

Conclusions

Comparison of the experimental data with model predictions shows that humic-bound metal ions can be released rapidly as free metal ions as a result of changes in acidity and ionic strength in the aqueous medium. LIPSMIS has yielded
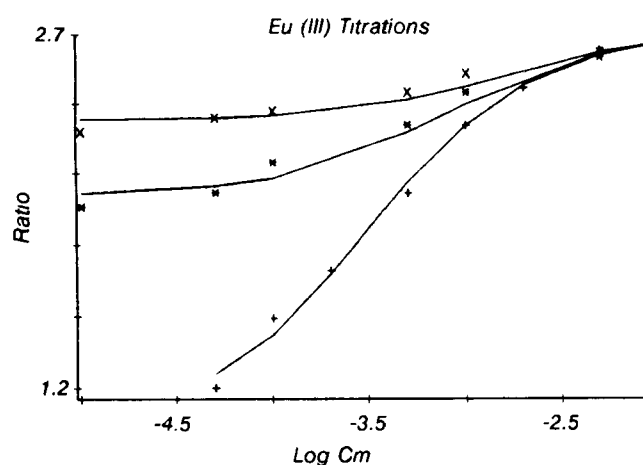

Figure 1. Ratio is the fluorescence rate = I_{592}/I_{616}. Cm is the total metal added. × = pH of 2.5. * = pH of 3.0. + = pH of 3.5. Humic concentration of 20 ppm.
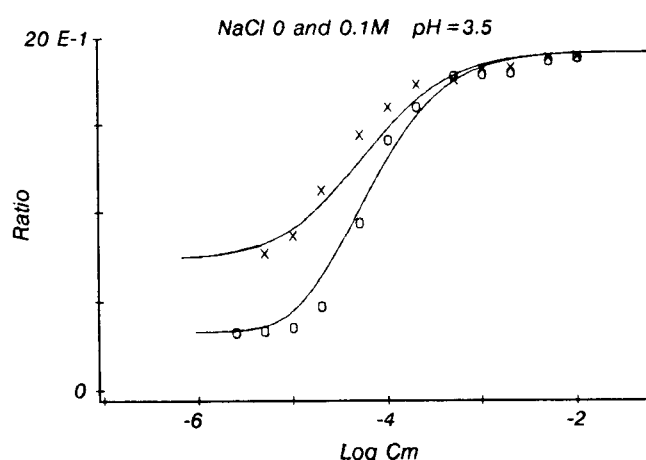

Figure 2. Humic concentration 20 ppm. O = no NaCl × = 0.1M NaCl pH = 3.5.

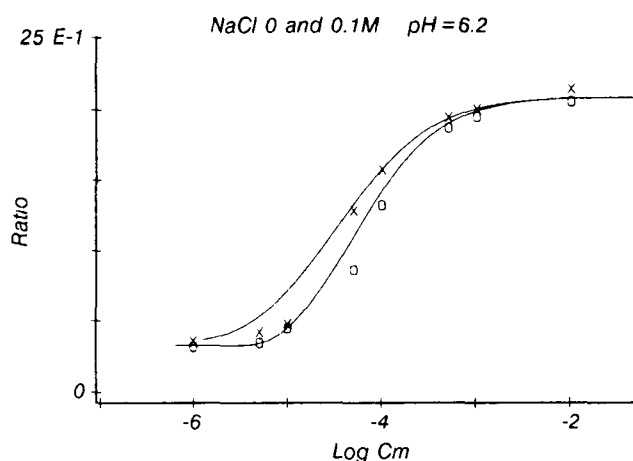Figure 3. Humic concentration 20 ppm. O = no NaCl × = 0.1M NaCl pH = 6.2.

reasonable values for the humic complexation capacity, C_L (1.5 × 10⁻³ meq/g of SRDOM). Addition of environmentally important metal ions such as Pb or Al results in competition for binding sites with the probe metal and an observable release of Eu. The ability to model and measure competitive metal binding allows this technique to determine the binding strengths of metals that are difficult if not impossible to measure by other techniques, e.g. Al(III). To date we have measured the mean Log K_i values of three metals: $\mu_{Eu} = 6.4$, $\mu_{Pb} = 4.8$, and $\mu_{Al} = 5.5$.

For more immediate application, portions of the model, which have been verified to the extent shown in this paper, will be incorporated into MINTEQA2 to allow an estimation of metal-natural organic binding, thus providing a more accurate prediction of metal speciation and fate.
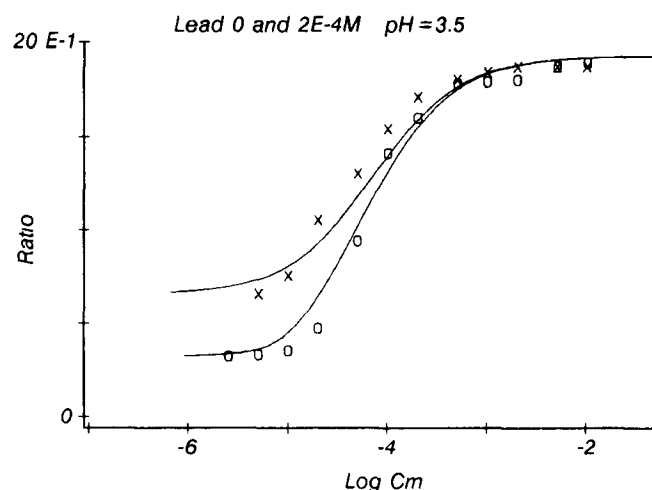

Figure 4. Humic concentration 20 ppm. O = no Pb(II) × = 0.0002M Pb(II) pH = 3.5

References

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