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Thermospray Mass Spectrometry Ionization Processes Fundamental Mechanisms for Speciation, Separation and Characterization of Organic Complexants in DOE Wastes

Dr. John E. Caton
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6120
Phone: 423-241-5189
E-mail: jec@ornl.gov

Debra T. Bostick
Oak Ridge National Laboratory
MS 6201
P.O. Box 2008
Oak Ridge, Tennessee 37831
Phone: 423-576-6201
E-mail: dab@ornl.gov

Peter W. Carr
University of Minnesota
207 Pleasant Street SE
Minneapolis, Minnesota 55455-0421
Phone: 612-624-0253
E-mail: carr@chem.umn.edu

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Research Objective

The overall objective of this research is to develop and enhance our understanding of the chemical equilibria for major organic complexant species and their products with metals in an aqueous mixture such as the mixtures of DOE stored wastes. Our approach to achieving this objective is a series of incremental studies involving cooperative efforts at Oak Ridge National Laboratory and at the University of Minnesota. Investigations at ORNL are characterizing soft ionization mass spectrometry processes for the complexant species by developing and interpreting positive and negative ion thermospray mass spectrometry of some organic complexants and their decomposition products and relating the spectral distributions to gas phase chemistry. Subsequently this knowledge of the gas phase chemistry will be related to known solution chemistry behavior. At the University of Minnesota liquid chromatography separations on zirconia-based chromatographic supports (including bare zirconia dynamically modified with Lewis bases and PEI-coated zirconia) are being studied in order to understand the separation of organic complexants and the products formed by complexants with metals in complex aqueous mixtures; and thereby define the conditions needed to introduce a simplified chemical stream into the mass spectrometer. Ultimately, the knowledge gained from these parallel efforts will be combined at Oak Ridge National Laboratory to characterize the complexant species in a multi-component aqueous mixture with the final objective being to develop data needed to define chemical equilibria for complexant species in such multi-component mixtures.

Research Progress and Implications

This is a three-year project which started on October 1, 1997. This report summarizes the progress achieved for the first eight months of the study (through May, 1998). Thermospray positive ion mass spectra of seven different organic complexants have been defined in a water:methanol (1:1 by volume) solvent system that was buffered with 0.1 $\underline{M}$ ammonium acetate (pH = 6.7). These complexants were imidodiacetic acid (IDA), ethylenediamine-N,N'-diacetic acid (EDDA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Mass spectra of all these complexants showed a peak at mass $[M+1]^+$ when vaporized from this solvent medium. Only NTA showed a significant peak at mass $[M+18]^+$ which was interpreted as the formation of an adduct with an ammonium ion from the buffered solvent medium. This observation for the vaporized NTA is consistent with the measured acidity in aqueous solution where the first acid dissociation for NTA has a lower pK value than those reported for EDTA, HEDTA, and IDA (1). This tendency to form an ammonium adduct in the gas phase would indicate that NTA has a lower proton affinity than the other complexants in the vaporized phase. This lower proton affinity in the vapor phase would be consistent with the greater observed acidity in the solution phase. Accordingly, this observation provides an indication that characteristics observed after thermospray vaporization may aid in defining behavior in solution. Such interpretations of thermospray mass spectra should be useful in the characterization of DOE mixed waste solutions.

Progress has also been made in developing thermospray mass spectra at source temperatures of less than 170° C. Such lower source temperatures should reduce the amount to thermal degradation for labile species. Pressures in the analyzer chamber of the mass spectrometer tend to elevate as the thermospray source temperature is reduced; however, the instrument has been operated for up to 8 hours at a source temperature of 175° C and a solvent flow of 1 ml/min. This time interval is of sufficient duration to analyze multiple liquid chromatography separations.

(1) Ringbom, A., "Complexation in Analytical Chemistry". Volume XVI in Chemical Analysis, (P.J. Elving and I.M. Kolthoff, eds), Interscience Publishers, New York, 1963.

Planned Activities

The subcontract to provide for the collaborative studies at the University of Minnesota has only recently been established (May 1998). Thus activity at both ORNL and the University of Minnesota will greatly intensify during the next four months with the planned schedule as follows:

—07/98: Complete evaluation of relative proton affinities and gas phase acidities of organic complexants after thermospray vaporization
—12/98: Complete separation studies on bare zirconia dynamically modified with Lewis bases.
—03/99: Evaluate predictive capability of proton affinity/gas phase acidity/TSMS characteristics
—09/99: Complete study of chromatographic properties of PEI-coated zirconia.
—11/99: Complete TSMS studies of some known chemical species of complexants and metal ions.
—09/00: Complete manuscripts for open literature describing results of these studies.

Other Access To Information

Results from these investigations will be published in the open literature. At this point in time only minimal resources have been expended and no publications have been generated.