MASTER

CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY

Progress Report
for Period November 1, 1977 - July 31, 1978

Henry Freiser

University of Arizona
Tucson, Arizona 85721

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

August 1978

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY

Progress Report

for Period November 1, 1977 - October 31, 1978

ABSTRACT

During the current contract period, the high susceptibility of lanthanide chelate stability to steric hindrance was confirmed. The increase in coordination number of lanthanides from lanthanum to ytterbium as evidenced from extraction equilibria serves to increase their separability. 8-Quinolol immobilized on silica can separate lanthanide ions.

PROGRESS REPORT

During the current contract period, the research conducted generally followed the course indicated in the original proposal and complied with the contract requirements. As mentioned in our last progress report (C00-4073-1), a serious obstacle impedes the full exploitation of the pattern recognition approach to design of extractants of improved selectivity; namely, the glaring deficiencies in chelate stability constant data for lanthanides (as well as for many other groups of metals) in the literature. Therefore, during this period the greatest attention was paid to exploring ideas developed or hinted at in our earlier work.

Inasmuch as the abstract factor analysis study (1) indicated that, in the EDTA family at least, substituents inducing steric hindrance

to chelation seemed to enhance the chelate stability difference between the lanthanide ions, we decided to compare the behavior of 8-quinolinol (oxine) and its 2-methyl derivative. Three experimental approaches have been employed:- (a) Potentiometric determination of lanthanide-2-methyl-oxine chelate stability constants, (b) Solvent extraction equilibrium determination of the lanthanide-oxine and-2-methyloxine systems, and (c) Chromatographic examination of oxine immobilized on silica.

While our previously described automated potentiometric chelate stability constant apparatus functioned satisfactorily, measurements on the lanthanide-2-methyloxine system did not yield reliable values for stability constants. This problem arose because the chelates did not form at a sufficiently low pH to avoid metal ion hydrolysis, even when the initial ligand concentration was raised. We also synthesized 5,7-dichloro-2-methyloxine whose lower pK_a resulted, as expected, in a lower pH of chelate formation, and accessible stability constant values. Some anomalies in the results remain, but they seem interesting enough to warrant redetermination.

These experiments did dramatically demonstrate the validity of our hypothesis concerning the susceptibility of lanthanides to steric hindrance in ligands. Furthermore, our experiments do serve to yield maximum upper limits to the possible values of the chelate stability constants.

Inasmuch as the 8-quinolinol family of ligands appear to have promise for selective separation of the lanthanides, a solvent extraction study of the behavior of oxine and 2-methyloxine with selected lanthanides

has gotten under way. From the extraction equilibrium data, it appears that the log D (distribution ratio) of La^{3+} varies with the third power of $\log [\text{HOx}]_0$ while that of Yb^{3+} varies with the sixth power. This not only means that the formulas of the extracted species vary, i.e. they are La O_3 and $\text{Yb}(\text{Ox})_3 \cdot 3\text{HOx}$, respectively, but, more importantly from a separations point of view, that the selectivity of oxine for the La-Yb pair and probably for the lanthanide ions as a group, increases with increasing extractant concentration. In the next period we plan to further explore the oxine and 2-methyl oxine systems and, moreover, to examine the behavior of KELEX 100, a commercial oxine-like extractant, in the same manner.

The investigation of the behavior of oxine when it is chemically bonded to a silica surface was undertaken as an alternative approach to lanthanide separation to the reversed phase liquid chromatography referred to earlier. As a result of our study, the first involving true chromatographic behavior (as opposed to column washing) of an immobilized chelating agent, it was found possible to easily separate a number of lanthanide ions. Two papers (2, 3), appended to this progress report, have been submitted to Analytical Chemistry. This work shows great promise and will be further investigated - by preparing and evaluating behavior of other, selected, immobilized chelating agents.

Reprints Removed

Literature Cited (copy appended)

1. D. L. Deuwer and H. Freiser. "Relating Molecular Structure to Metal Chelate Stability and Reagent Selectivity: Abstract Factor Analysis of the Chelate Formation Equilibria for Some Diaminetetracarboxylic Acids", Anal. Chem., 49, 1940 (1977).
2. J. R. Jezorek and H. Freiser, "Metal-Ion Chelation Chromatography on Silica-Immobilized 8-Hydroxyquinoline", in press.
3. J. R. Jezorek and H. Freiser, "A 4-(Pyridylazo)-resorcinol (PAR)-Based Continuous Detection System For Trace Levels of Metal Ions", in press.