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Progress Report

EXTRACTION OF INORGANIC SUBSTANCES BY ORGANIC SOLVENTS

Contract Number AT(30-1)-1663
AEC NYO-6550

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by

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Introduction

Based on experience gained in the study of the solvent extraction of ferric chloride under Contract AT(30-1)-562, it was believed that the methods and techniques developed could be applied along with radioactive tracer techniques to the study of solvent extraction of other inorganic halides. A period of several months lapsed between graduation of the experienced graduate students following termination of the ferric chloride study and initiation of the current study under Contract AT(30-1)-1663, however, so that the momentum of the earlier project was lost.

In order to minimize the delay in starting the experimental work, aluminum chloride was selected as the substance for investigation first. It was selected to provide indoctrination in the techniques of preparation, purification and handling anhydrous materials, measurement of absorption spectra, analysis for water in organic solvents, etc., because the materials were more readily available than for the chlorides of protactinium, niobium, and tantalum and ferric bromide. Investigation of the aluminum chloride system is still in progress. Work on the extraction of bromides is also underway at this time. Experimental investigation of the extraction of the chlorides of protactinium, niobium, and tantalum has not been started, but it is expected that work on protactinium will be started in a few weeks.

Status of the Program

1. Aluminum Chloride

The behavior of aluminum chloride in the presence of organic solvents commonly used for solvent extraction is of interest because aluminum chloride cannot be readily extracted from aqueous solution. In the cases of the extractible chlorides of iron and gallium it is known that the form extractible from aqueous hydrochloric solution is a complex tetrachloro acid, i.e., $HFeCl_4$ and $HGaCl_4$. Water extracts with these acids. Existence of the analogous acid $HAlCl_4$ in certain systems of interest in organic chemistry has been postulated although it is a rather controversial point.

The experimental work underway has been directed toward finding out why aluminum chloride does not extract although it forms some halide complexes similar to those formed by extractible elements. The approach is that of studying the effect of the addition of hydrogen chloride and water, separately and together, to anhydrous solutions of aluminum chloride in diethyl ether. Light absorption measurements and chemical analyses of phases which separate are being used to measure the effects. Conductance measurements will also be used.

An existing stainless steel drybox has been overhauled and equipped with a new source of dry air and a means for circulating air within the box. A high vacuum system for purification of anhydrous halides by sublimation has been constructed. Analytical procedures for the determination of aluminum, chloride, and water have been developed.

Results obtained so far are as follows:

a) The preparation of a pure, stable, anhydrous solution of aluminum chloride in diethyl ether is in itself rather difficult. Several methods have been tried. Solutions prepared by mixing the materials at room temperature discolor slowly and show an increase in ultraviolet absorbency with time. The most satisfactory method of preparation involves the mixing of aluminum chloride and diethyl ether at dry ice temperature to form the solid monoetherate, adding the latter to diethyl ether at dry ice temperature, allowing the mixture to warm slowly to dissolve the etherate, discarding a small amount of heavy reddish colored phase, and storing the colorless ether layer for use. Soltuions prepared in this way do not discolor on standing and have the simplest ultraviolet absorption spectrum. One such preparation consisted of a solution which was 0.0176 molar in aluminum chloride and had a single ultraviolet absorption band at 232 millimicrons not present in the ether.

b) Vacuum sublimation of the reagent grade aluminum chloride produced a material completely soluble in ether in contrast to the starting material.

c) In preliminary experiments it has been found that the addition of dry hydrogen chloride to an ethereal solution of aluminum chloride increases the ultraviolet absorbency but does not cause a change in the spectrum.

d) Addition of moist ether containing a known quantity of water produces no effect at first but after the introduction of an amount of water equivalent to 0.37 times the number of moles of aluminum chloride present, a flocculent white precipitate begins to form. Precipitation continues as more moist ether is added. Partial removal of aluminum chloride from the ether solution by the addition of small amounts of water does not appear to alter the ultraviolet absorption spectrum appreciably.

e) Addition of excess water removes the aluminum chloride from the ether layer without hydrolysis, apparently, as shown by analysis. Two clear liquid phases result.

f) Infrared absorption of an ethereal solution of aluminum chloride differs from that of a pure ether only slightly with respect to the intensities of a few bands.

g) For reference, the infrared absorption spectra of solid aluminum chloride hexahydrate, aluminum oxide, and aluminum oxide hydrate incorporated in plates of potassium bromide have been measured.

2. Protactinium Chloride

It is hoped that the arrangements with the AEC Isotopes Division and the Oak Ridge Office of the Research Division for procurement of protactinium-233 will be completed shortly so that experimental work can be started within a few weeks.

3. Bromides

Preliminary experiments leading to a study of (1) the factors affecting the solvent extraction of ferric bromide from aqueous solutions and (2) the differences between chloride and bromide systems are being conducted.

Hydrobromic acid has been purified by distillation and standard solutions have been prepared. Since spectrophotometric methods will be used to follow complex ion formation, the hydrobromic acid stock solutions have been examined in the ultraviolet spectral region. It has been found that the purified hydrobromic acid contains an impurity which absorbs strongly in the ultraviolet. The absorption increases with time. The impurity does not appear to be bromine but it can be extracted into ether leaving a stable hydrobromic acid solution. The hydrobromic acid itself, unlike hydrochloric acid, does not extract into ether.

When satisfactory hydrobromic acid has been prepared, it will be used for the synthesis of ferric bromide. Low actinic glassware has been obtained for storage of ferric bromide solutions.