JUL 15 1963

UNCLASSIFIED

MASTER

NYO-6551

Progress Report

EXTRACTION OF INORGANIC SUBSTANCES BY ORGANIC SOLVENTS

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

November 1, 1954 to July 1, 1955

by

H.M. Clark

Facsimile Price $ 1.60
Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Walker Laboratory
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York

Issued: July 15, 1955

UNCLASSIFIED

NYO-6551

Progress Report on

EXTRACTION OF INORGANIC SUBSTANCES BY ORGANIC SOLVENTS

TABLE OF CONTENTS

I. STATUS OF THE PROGRAM

1. Aluminum Chloride.- A study of the properties of the system aluminum chloride—diethyl ether—water—hydrogen chloride has been continued by Mr. D. E. Byrnes. Attempts have been made to establish a means for following the effect of addition of water and hydrogen chloride to anhydrous solutions of aluminum chloride in diethyl ether. Both light absorption and conductance measurements have been made.

Early measurements gave encouraging evidence of a weak characteristic ultraviolet absorption spectrum for anhydrous aluminum chloride—diethyl ether solutions. The spectrum was not reproducible, however, and after considerable examination it was concluded that the difficulty was instrumental and was probably complicated by fluorescence. Ultraviolet absorption measurements were abandoned as a means of following complex formation and changes of species in solution for the anhydrous aluminum chloride—ether solutions.

As another approach, the variation of electrical conductance of dilute anhydrous aluminum chloride—diethyl ether solutions with dilution and with addition of water was studied. The effect of dilution is represented by the curve in Fig. 1. Upon the addition of measured quantities of water, in the form of wet ether, the conductance for essentially constant aluminum concentration varied as shown in Fig. 2. As previously reported the addition of water leads eventually to the formation of a white solid. This solid has been identified as $AlCl_3 \cdot 6H_2O$.

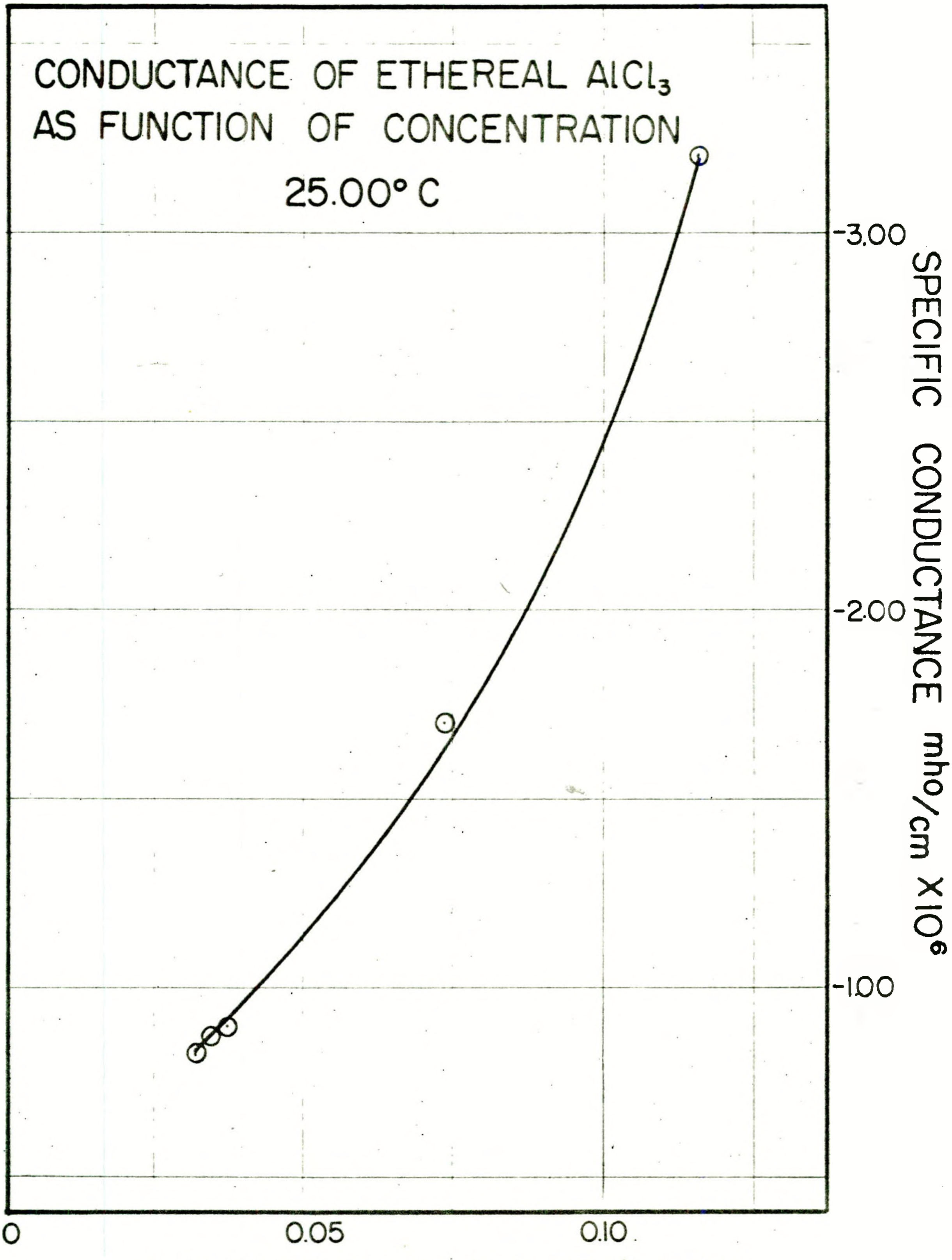
CONDUCTANCE OF ETHEREAL AlCl₃
AS FUNCTION OF CONCENTRATION
25.00° C
-3.00
-2.00
-1.00
SPECIFIC CONDUCTANCE mho/cm X10⁶
0
0.05
0.10
CONCENTRATION MOLES / LITER

Fig. 1.

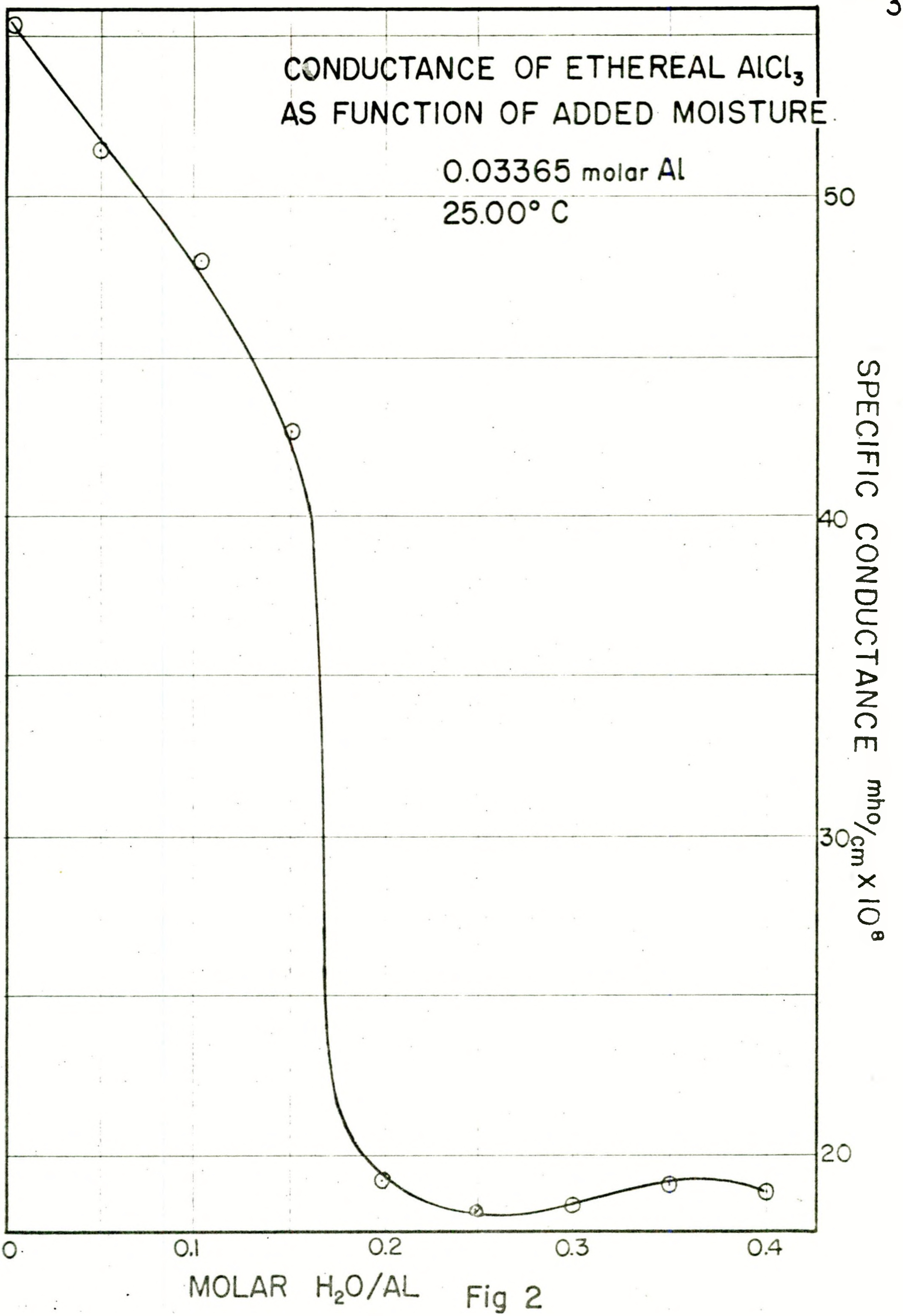
CONDUCTANCE OF ETHEREAL $AlCl_3$
AS FUNCTION OF ADDED MOISTURE
0.03365 molar Al
25.00° C
50
40
30
20
SPECIFIC CONDUCTANCE $mho/cm \times 10^8$
0
0.1
0.2
0.3
0.4
MOLAR H_2O/AL

Fig 2

The conductance work is to be extended to include solutions containing hydrogen chloride.

Throughout the investigation of the aluminum chloride—diethyl ether system there has been interference arising from decomposition of the ether by aluminum chloride. Dark red solutions form regardless of the purity of the ether or the aluminum chloride. A colorless sample of the etherate was obtained by vacuum distillation of the usual dark-brown solid obtained by crystallization from a concentrated solution cooled to about -10°C. The infrared spectrum of this solid has been measured with a Perkin-Elmer double beam instrument acquired by the Chemistry Department during the last year. The spectrum differs markedly from that of either aluminum chloride or diethyl ether alone.

Infrared absorption spectra for other solid hydrated halides of aluminum have been measured for comparison with the aluminum chloride spectrum. A correlation of analagous bands is being attempted.

Anhydrous ether solutions prepared from the purified solid became colored on standing at room temperature. Apparently the formation of substances which interfere with spectrophotometric measurements is associated with cleavage of the ether by aluminum chloride. A similar effect occurs with isopropyl ether. Aluminum chloride has turned out to be a less sttractive solute than the ferric chloride studied previously.

The ferric chloride—ether system and the aluminum chloride—ether system may be compared as follows:

(1) Anhydrous aluminum chloride interacts (solvation) more strongly with ether than anhydrous ferric chloride does.

(2) In the presence of water and in the absence of hydrogen chloride both aluminum chloride and ferric chloride prefer solvation by water rather than ether.

(3) In the presence of excess chloride ion ferric chloride forms a tetrachloro complex in aqueous solution. This complex is extractible by ether in the presence of hydrogen ions or lithium ions. Water is, in fact, essential for the extraction of the complex. In the case of aluminum chloride, however, it appears that a tetrachloro complex does not form in aqueous solution containing the strongly hydrated aluminum ion.

In the current work conditions are being sought under which an aluminum tetrachloro complex can be formed, by the addition of hydrogen chloride. It is hoped that this phase of the study and the aluminum chloride work as a whole will be completed in the next two months.

2. <u>Protactinium Chloride</u>.- A second graduate student, Mr. D. E. Neil, is currently associated with the solvent extraction study. His association with the program was informal during the second semester of the academic year but is now formal during the summer months. A survey of the unclassified literature on protactinium was completed pending the granting of the required Q clearance to Mr. Neil. Experimental work is now underway.

Preliminary work on the separation and purification procedures for protactinium has been conducted using the 6-hour Pa^{234}(UZ) obtained in extremely small amounts from uranyl nitrate. Approval has been obtained for irradiation of metallic thorium to produce the 27-day protactinium-233. Thorium has now been irradiated in the Brookhaven reactor and separation of the protactinium-233 is underway.

The beta-gamma emitting protactinium-233 will be used to study the values of and the factors affecting the extraction of protactinium from aqueous chloride solution. Included will be the effect of bromide and fluoride ions.

3. Ferric Bromide.- During the three summer months of 1954 a graduate student, Mr. A. J. Hogan, started experimental work on the ferric bromide system. Preliminary measurements of the extraction of hydrogen bromide from aqueous solution by diethyl ether were made. In addition the visible and ultraviolet spectra of hydrobromic acid were examined. As for the aluminum chloride work, erratic behavior of the spectrophotometer caused some difficulties. When reproducible spectra were obtained it was found that the hydrobromic acid purified by distillation contained a contaminant which complicated the spectrum.

Several methods of preparation of an aqueous solution of ferric bromide were investigated. The most satisfactory one consists of dissolving pure iron wire in hydrobromic acid containing the proper amount of bromine as oxidant.

Another graduate student, Mr. G. S. Golden, expressed an interest in the solvent extraction study and, in particular, in continuing the work on bromides for his Ph.D. thesis. He has not been formally associated with the program and his academic schedule did not allow much free time. During the year, however, he has (1) read the pertinent literature, (2) studied the purification of hydrobromic acid experimentally, (3) found good evidence that the impurity observed in the earlier work was the tri-bromide ion, (4) prepared a sample of ferric bromide from elemental iron, and (5) made a preliminary examination of the visible spectrum of ferric bromide in hydrobromic acid.

It is hoped that Mr. Golden can be formally associated with the program this fall to continue the study of the extraction of inorganic bromides.

4. Tantalum Chloride.- Experimental work on tantalum chloride has been underway since early last semester. The work is being carried out by Mr. A. Behringer, a graduate student not formally associated with the program but working on this one phase for his master's thesis.

Consideration has been given to various methods of preparing aqueous tantalum chloride solutions from the starting materials available. In the initial experiments fluoride ion is present to stabilize the solutions. Work is underway to obtain fundamental information on the published extraction methods used for tantalum by the U.S. Bureau of Mines.

5. Ruthenium Chloride.- Small quantities of elemental ruthenium and ruthenium compounds have been obtained. In addition, an application for procurement of a sample of 1 year radio ruthenium-106 has been filed.

As soon as a man becomes available for work on ruthenium the solvent extraction behavior of ruthenium chloride will be studied not only with respect to the value of the organic solvent and the composition of the aqueous solution, but also with respect to the oxidation state of ruthenium.

6. Niobium Chloride.- During the past year an undergraduate student studied the preparation of pure niobium-95 tracer by ion exchange enthods. This was in anticipation of finding a man to conduct the solvent extraction study on niobium chloride.

II. APPROXIMATE STATEMENT OF EXPENSES

Period of November 1, 1953 to October 31, 1954

	Salaries	Indirect Charges	Materials, Supplies, etc.	Total
AEC	$3580	$ 568	$2137	$6285
RPI	900	2255	....	3155
Total	$4480	$2823	$2137	$9440

Period of November 1, 1954 to July 31, 1955

	Salaries	Indirect Charges	Materials, Supplies, etc.	Total
AEC	$2520	$ 375	$1551	$4446
RPI	675	1414	....	2089
Total	$3195	$1789	$1551	$6535

Estimate for Period of August 1, 1955 to October 31, 1955

	Salaries	Indirect Charges	Materials, Supplies, etc.	Total
AEC	$1155	$ 125	$ 500	$1780
RPI	225	648	...	873
Total	$1380	$ 773	$ 500	$2653