90
6-23-80

DR. 1371

ornl

ORNL/TM-7240

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

MASTER

A Solvent Extraction Study of the Thorium Nitrate, Nitric Acid, and Tributyl Phosphate–Dodecane System: Density and Acidity Relationships

A. J. Weinberger
J. L. Marley
D. A. Costanzo

This document is
PUBLICLY RELEASABLE
Dave Hamrin, ORNL
Authorizing Official
Date 4-29-11

STET

~~APPLIED TECHNOLOGY~~

~~Any further distribution by any holder of this document or of the data therein to third parties representing foreign interests, foreign governments, foreign companies and foreign subsidiaries or foreign divisions of U. S. companies should be coordinated with the Director, Division of Nuclear Power Development, Department of Energy.~~

RELEASED FOR ANNOUNCEMENT IN ALDR.
Distribution limited to participants in the
Consolidated Fuel Reprocessing Program.
Others request from Program Mgr.
CFRP, OROO.

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
the Department of Energy
Technical Information Center
P.O. Box 62, Oak Ridge, Tennessee 37830
Printed Copy A03 ; Microfiche A01

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

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.

ORNL/TM-7240
Dist. Category UC-86

Contract No. W-7405-eng-26

Consolidated Fuel Reprocessing Program

A SOLVENT EXTRACTION STUDY OF THE THORIUM NITRATE, NITRIC ACID, AND TRIBUTYL PHOSPHATE–DODECANE SYSTEM: DENSITY AND ACIDITY RELATIONSHIPS

A. J. Weinberger
J. L. Marley
D. A. Costanzo

Analytical Chemistry Division

Date Published: May 1980

DISCLAIMER

This book 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.

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

~~RELEA~~ [illegible] T IN ALDR.
~~D~~ [illegible] ~~ants in the~~
~~Con~~ [illegible] ~~Program.~~
[illegible] ~~gram Mgr.~~
[illegible] ~~ORO).~~

CONTENTS

HIGHLIGHTS

A solvent extraction study to determine equilibrium conditions of thorium nitrate-nitric acid with 30% tributyl phosphate in normal dodecane has been completed. Experimental conditions studied were 30 to 60°C, 0.05 to 1.5 *M* $Th(NO_3)_4$, and 0.0 to 3.0 *M* HNO_3. The extractant concentration was constant at 30% tributyl phosphate.

The equilibrium experiments have produced data which demonstrate that thorium nitrate concentration, free acid, and density are related in equilibrium behavior between the aqueous and organic phases from 30 to 60°C in the 30% tributyl phosphate-dodecane solvent extraction system. The concentration interactions apply to both the two- and three-phase regions.

A linear correlation was observed for the density (D) of the aqueous or organic phase and the concentration of thorium and free acid. The general form of the equation is $D = a(C_{Th} + bC_H) + c$, where a is the slope, b is a constant, c is the intercept, and C_{Th} and C_H are the molar concentrations of thorium and free acid respectively.

The relationship of temperature, thorium nitrate, and free acid makes possible the definitions of the boundaries between the two- and three-phase regions. This dependence, in turn, permits operational control or simulation studies of the system within the two-phase region. The data demonstrate the interactions of the components of the Thorex system and can be used to improve the mathematical description of equilibrium in the SEPHIS-Thorex computer program.

1. INTRODUCTION

Laboratory equilibrium data with the solvent extraction system, thorium nitrate-nitric acid-tributyl phosphate (TBP) in normal dodecane (NDD) were needed to support further development of the acid Thorex flowsheet utilizing 30% TBP in NDD as an extractant. Earlier laboratory and pilot plant studies of the separation of thorium and uranium by the Thorex process[1-5] paralleled the development of plutonium and uranium separations by the Purex process and evolved an extensive technical base for both solvent extraction systems utilizing TBP as an extractant.

One significant development to further the study of the application of the Purex process to the separation of plutonium and uranium in liquid-metal fast-breeder reactor (LMFBR)-type fuels has been the solvent extractive processes having interacting solutes (SEPHIS) computer program.[6] The SEPHIS program allows, with accuracy and reliability, the prediction of stage and product stream concentrations, thus reducing the number of experimental runs required to establish optimum flowsheet conditions.

A modification of SEPHIS, the SEPHIS-Thorex program, was designed for application to the acid Thorex flowsheet.[7] Supporting data for the mathematical model developed for SEPHIS-Thorex was desirable; therefore, an experimental program was designed to fill the need. A program of equilibrations of 0.05 to 1.5 *M* thorium nitrate and 0.0 to 0.3 *M* HNO_3 with 30% TBP in NDD was set. Temperatures of 30, 40, and 60°C were selected for the equilibrations. These conditions bracket the flowsheet parameters of the acid Thorex system.

2. EXPERIMENTAL

2.1 Reagents

Practical-grade normal dodecane (NDD), Eastman Kodak catalog number P2556, was used without further purification. The NDD was determined free of detectable organic impurities by an ASTM analysis procedure for boiling range distribution of petroleum fractions by gas chromatography.[8]

Commercial grade tributyl phosphate (TBP) was purified by distillation under reduced pressure for the removal of water and most of the hydrolysis products. After distillation, the TBP was stored in brown bottles in subdued light.

The 30% tributyl phosphate in normal dodecane extraction mixture (TBP-NDD) was prepared by volume mixing of the above reagents. Prior to its use as a reagent, the solution was further purified by stirring for 10 min with an equal volume of 0.5% sodium carbonate, and then was filtered through Whatman 42 paper into a brown bottle for storage. This extraction reagent was analyzed by gas chromatography and determined to contain less than 0.01% monobutyl or dibutyl phosphate.[9]

The thorium nitrate, nitric acid, and other reagents were reagent-grade chemicals. Confirmations of purity levels were made by chemical and spectrographic methods. The water used for reagent preparation was double-distilled.

Initially, a 2.384 *M* thorium nitrate solution was prepared by dissolving $Th(NO_3)_4 \cdot 4H_2O$ crystals in water and then diluting to a 1-ℓ volume at ambient temperature. Aliquots were taken and analyzed by the EDTA titration method[10] to verify concentration.

Nitric acid for solution preparation was standardized from dilutions of reagent nitric acid (sp gr 1.42). Dilutions to approximately 13 and 5 M HNO_3 each were made with distilled water; the concentration of each was then established by potentiometric titration with standardized 0.1 M sodium hydroxide. Final concentrations of the nitric acid solutions were 13.05 and 4.950 M HNO_3 respectively.

A density determination of the 2.384 M $Th(NO_3)_4$ solution was made (according to the pycnometer procedure described later) in preparation for the transfer of weighed aliquots of the stock solution. The weight of solution calculated to contain the thorium required for each aliquot was weighed into tared 200-ml volumetric flasks. The required standardized nitric acid was added volumetrically; the solutions were then diluted to volume with water. Weight transfer was used because of the better accuracy attainable, particularly when aliquoting concentrated, viscous material.

2.2 Apparatus

A constant temperature water bath and an extraction vessel with a jacket for recirculating the water were assembled for the studies. The bath assembly, which was used for experiments at 30°C, was based on a 20-ℓ (5-gal) container insulated with asbestos tape. The water was circulated with a motor-driven stirrer. Quartz-jacketed 125- and 500-W immersion heaters were controlled with a Philadelphia microset mercury regulator and a Lapine electronic relay. The bath maintained temperature to within ±0.1°C. The water-jacketed glass extraction vessel was used for the 40 and 60°C equilibrations. The apparatus was fabricated 2.2 × 17-cm long, with a sample volume of about 65 ml. Temperature, which was monitored at a thermometer well located in the water outlet, was controlled by a precision mercury regulator in an attached Haake-type thermostated circulating water bath. Control of this bath and the reaction vessel was also maintained to ±0.1°C. The jacketed extraction vessel design permitted clear sample observation with no upset in temperature.

An International clinical centrifuge, model CL, was mounted in a Modern Equipment Company model 25-SR oven. The centrifuge was supported in the oven by means of a ¼-in.-thick perforated stainless steel plate. The temperature-controlled centrifuge was set up to completely separate any suspended organic material from the aqueous phase while maintaining the equilibration temperature.

Kimax 10-ml specific gravity bottles with side arms were used for density determinations of the aqueous and organic phase samples at 30, 40, and 60°C. Density measurements of samples from incipient third-phase experiments (described below) were performed using a calibrated and tared 750 μl pipette. The 750-μl pipette, rather than the 10-ml pycnometer, was used for the density measurements because of the extreme care necessary to avoid erroneous results. Organic samples, which were near the third-phase transition (those from elevated temperature equilibrations), were subject to precipitation if they were not carefully and quickly handled while maintaining the temperature.

Other equipment used for these studies was of a quality consistent with the analytical accuracy required.

2.3 Detailed Experimental Procedures

2.3.1 Solution matrix design

A matrix of thorium nitrate-nitric acid solutions was devised to permit equilibrations in the two- and three-phase regions. The thorium nitrate solutions, made from $Th(NO_3)_4 \cdot 4H_2O$, were prepared to contain 0.05 to 1.5 M thorium. The designations and concentrations of these solutions are as follows: solution A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.00 *M*; H, 1.25 *M*; and I, 1.50 *M*. Nitric acid was added during preparation to provide solutions with 0.0 to 3.0 *M* HNO_3.

Table 1 shows the plan for concentrations of all solutions. These solutions shall be referred to in this report as starting solutions.

Table 1. Matrix of aqueous thorium nitrate-nitric acid solution sets prepared as starting solutions for an equilibration study

Free acid, *M*	Thorium concentrations, *M*								
	A 0.05	B 0.10	C 0.20	D 0.30	E 0.50	F 0.75	G 1.00	H 1.25	I 1.50
0.0	X		X		X		X		
0.05		X						X	
0.10	X		X		X		X		X
0.25				X					
0.50	X		X		X		X		X
0.75						X			
1.00	X		X		X		X		X
1.50		X						X	
3.00	X		X		X		X		X

2.3.2 Normal phase separation

The normal phase separation is the separation after an equilibration into clearly defined aqueous and organic phases. When there was a two-phase system (one distinct aqueous phase and one organic phase), the aqueous and organic phases were separated and analyses were made. When there was a three-phase system, two organic phases were present after an equilibration and phase separation. The aqueous phase was first removed and analyzed; the combined organic phases were then diluted with an equal volume of TBP-NDD to obtain a clear single phase. The single phase was then analyzed, and the results were corrected for dilution.

To perform an extraction and analysis, 15 ml of the starting solution was pipetted into a sample container suspended in a 30°C constant temperature water bath. Fifteen milliliters of TBP-NDD was added, and 10 min was allowed for thermal equilibrium. To guard against the evaporation of water and NDD, the vessel was loosely sealed with Parafilm M; the mixture was then stirred for 5 min with a Teflon stirrer at sufficient speed to produce a uniform dispersion. To prevent evaporation throughout the stirring period, a disk, which acted as a cover on the extraction vessel and as protection against solution loss caused by splashing, was attached to the stirrer. The phases were allowed to separate for about 5 min after this stirring step and were then visually inspected to determine whether a two- or a three-phase condition existed. Data from the observation was recorded.

The aqueous phase was transferred to a centrifuge tube and sealed with Parafilm M. The sample was centrifuged for 15 min at 30°C to separate any organic material remaining in the aqueous phase.

A portion of the aqueous solution was transferred from the tube to fill a calibrated pycnometer suspended in the water bath to obtain thermal equilibrium. After adjusting the volume of liquid in the pycnometer at equilibrium temperature, the pycnometer was wiped and dried, cooled to room temperature, and weighed. The density calculation was made from the weights and the known volume of the pycnometer.

The aqueous solution from the density measurement was used to determine the thorium and free-acid concentrations. Thorium was determined by the EDTA titration method[10] when the quantity of thorium was within the range of the method (1–100 mg Th), or it was determined by the Arsenazo III photometric method[11] when the thorium was present in microgram quantities. The free acid was determined by a potentiometric titration in an oxalate medium.[12,13]

The density of the organic layer from a single-phase organic separation was determined first and then followed by an analysis for thorium and free acid.

Only clear single-phase samples are suitable for a representative thorium or free acid determination; therefore, when the organic layer contained two phases, as evidenced by either a clearly defined meniscus or a separable layer prior to analysis, the two organic layers were converted to a single phase by dilution with 15 ml of TBP-NDD. The resulting single-phase organic layer was brought to thermal equilibrium at 30°C for density, thorium, and free acid measurements. In the final calculations, consideration was given to dilution.

2.3.3 Incipient three-phase experiments

The incipient third-phase (ITP) condition is a boundary or transition condition between the two- and three-phase systems. It is seen as a slight clouding of the organic layer – a clouding which does not separate into a distinct meniscus within a normal separation time. The addition of a small amount of aqueous to a system in the ITP condition will result in a three-phase system. The addition of a small amount of TBP-NDD to a system in the ITP condition will result in a two-phase system with clear aqueous and organic phases.

The ITP experiments, therefore, were performed on the solution concentrations in which the equilibration (described in Sect. 2.3.1) produced three phases, or a cloudy layer without clear evidence of organic third-phase formation within the normal separation time. To perform the experiment, a known quantity (nominally 15 ml of the starting solution) was pipetted into a water-jacketed extraction vessel. An equal volume of TBP-NDD was added, and the mixture was stirred for 5 min at 30°C. The TBP-NDD was then added in controlled increments of 0.5 to 1.0 ml, with thermal equilibration and stirring following each addition. As the two-phase organic layer approached clarity, additions were decreased to 0.1 to 0.2 ml until a clear single organic layer was obtained.

A confirmation of this endpoint was made as follows. About 0.25 ml of the aqueous starting solution was accurately measured, added to the above system, and mixed to reproduce the ITP condition. Incremental titrations of 0.10 to 0.20 ml of TBP-NDD were made until the clear system again appeared. The equilibrated aqueous and organic volumes (sample aliquot volume plus aqueous added for the titration and all corresponding volumes of TBP-NDD) were recorded for calculating the thorium and free acid. Corrections were made to obtain the thorium and free acid concentrations in the original 15-ml aqueous and organic aliquots.

The density of the organic phase was determined from the weight of organic contained in the calibrated and tared 750-μl pipette. Care was taken to bring the pipette to temperature by rinsing with thermal equilibrium solution. After the pipette was warmed to the equilibration temperature and filled to the volume mark, it was cleaned with a Kimwipe moistened with acetone. The pipette and contents were placed in a tared sample bottle for final weighing.

Observations made during the 30°C series resulting in a modification of the test procedure and equipment when applied to the 40 and 60°C equilibrations. The water-jacketed extraction vessel was used for all of the equilibrations performed at 40 and 60°C. It was determined that a complete separation of aqueous and organic phases occurred by normal settling. No organic was separated by centrifugation at temperature; therefore, the use of the centrifuge could be discontinued. All other techniques and experimental parameters described for the 30°C test series were used in the 40 and 60°C test series.

3. RESULTS AND DISCUSSION

3.1 Phase Separation

In preliminary work, the separation of phases was satisfactory qualitatively; that is, the aqueous layer of a TBP-NDD equilibration was normally clear and distinct and did not appear to contain any organic in excess of that in solution.[14] Nevertheless, it was decided that a 15-min treatment in a clinical centrifuge would be performed to test for organic suspended in an aqueous layer. The use of the centrifuge at the temperature of sample equilibrium was considered necessary to ensure that the separated organic was the result of the physical treatment and was not associated with a change in solubility because of change in temperature.

All samples equilibrated in the 30°C test series were treated by centrifugation following the normal separation described in Sect.2. It was observed that none of these samples showed any evidence of further material separation; there was neither evidence of separation of droplets nor of meniscus formation. The aqueous solutions remained clear throughout. This confirmation was deemed adequate, since there was no reason to believe that layer formation and separation at 40 or 60°C should be more difficult than at 30°C; therefore, the centrifuge was not used in the studies performed at 40 and 60°C.

3.2 Stability of Free Acid and Time of Sample Storage

Samples were analyzed and then retested to demonstrate that the level of free acid does not change within the laboratory testing time. The samples selected ranged from 0.09 to 2.7 *M* in free acid and 0.09 to 1.21 *M* thorium in the aqueous phase. The concentrations in the organic phase were 0.01 to 0.4 *M* free acid and 0.07 to 0.34 *M* thorium respectively.

Samples were tested under two sets of conditions: storage at room temperature and storage in a frozen condition. The samples for the room temperature experiment were equilibrated and separated at 30°C, analyzed for thorium and free acid the same day separated, and then sealed for later reanalyses. The reanalyses were performed randomly within a four-month period. The samples designated for storage in the frozen condition were separated at 30°C, analyzed, and then frozen at −12°C. For reanalyses, these samples were warmed to room temperature, sampled, and immediately refrozen. The testing of the frozen samples was completed within one month.

With the exception of one sample, designated No. 5 Aqueous (Table 2), there was a pattern of free acid content repeatability consistent with the reliability of free acid measurements for the entire study and consistent with the precision established by measurements of

Table 2. Stability of aqueous and organic free acid samples in storage prior to analysis

Sample	Individual determinations (*M*)				Free acid (*M*)
Free acid after storage at room temperature					
1 Aqueous	2.604	2.612	2.504	2.560	2.570 ± 0.028[a]
1 Organic	0.395	0.378	0.401	0.397	0.393 ± 0.007
2 Organic	0.038	0.038	0.036	0.036	0.037 ± 0.001
3 Aqueous	0.087	0.084	0.079	0.082	0.083 ± 0.003
3 Organic	0.015	0.016	0.015	0.015	0.015 ± 0.001
4 Aqueous	0.864	0.874	0.879		0.872 ± 0.006
4 Organic	0.127	0.127	0.127	0.124	0.126 ± 0.001
5 Aqueous	0.504	0.455	0.456	0.438	0.463 ± 0.020
5 Organic	0.045	0.050	0.050	0.049	0.049 ± 0.002
Free acid after storage by freezing at −12°C					
6 Aqueous	0.429	0.428	0.432		0.430 ± 0.002
6 Organic	0.067	0.068	0.069		0.068 ± 0.001
7 Aqueous	2.728	2.708			0.718 ± 0.010
7 Organic	0.313	0.326	0.322		0.320 ± 0.005
8 Aqueous	0.671	0.672			0.672 ± 0.001
8 Organic	0.104	0.103			0.104 ± 0.001

[a] Mean value ± mean deviation.

analytical controls analyzed prior to a test series. It was noted that in No. 5 Aqueous, the free acid content was significantly lower at three months than the value obtained when initially separated; however, the No. 5 Organic did not show a loss. Although expected to be least stable, the No. 5 Organic, in fact, showed a gain in free acid. Most likely the problem was in the original analysis. It was also observed that assuming the first analysis of each sample was unbiased, there was an equal number of deviations, both high and low, for the reanalyses. Therefore, it was concluded that no significant changes in the data occurred because of changes in the free acid content of either the aqueous or organic phases.

3.3 Material Balance for Thorium and Free Acid

The data for the thorium and free acid determinations were examined to ascertain that the analyses of the aqueous and organic layers represented the quantities of acid and thorium in the starting aqueous solutions. Recovery values for all experiments at 30, 40, and 60°C show that the average recovery was 101.4% for thorium in 107 samples and 100.6% for free acid in 84 samples. The data are presented in detail in Table 3, which shows that adequate experimental control was maintained for work at all three temperatures. There are less free acid samples than thorium samples because of the experiments with no free acid added.

The percentage recovery is based on milligrams of thorium found in the aqueous-plus-organic layers divided by the amount of thorium in the starting solution times 100. The percentage recovery of the free acid is based on milliequivalents of acid in the starting and final solutions.

Table 3. Experimental material balances for thorium and free acid concentrations

Experiment type	Free acid analysis			Thorium analysis		
			Two-phase			
Sample analyses	14	16	19	17	19	23
Recovery, %	100.4	99.0	100.0	99.1	101.1	101.2
Precision, %[a]	0.8	2.2	2.7	1.5	1.2	0.8
			Three-phase			
Sample analyses	9	5	5	12	7	7
Recovery, %	103.2	99.5	100.9	101.3	102.1	102.7
Precision, %	3.0	1.9	1.8	3.5	0.8	0.8
			Incipient three-phase			
Sample analyses	6	5	5	8	7	7
Recovery, %	101.2	101.6	103.6	102.1	104.7	102.4
Precision, %	2.6	4.9	3.8	1.4	1.0	2.8

[a] Precision expressed as one standard deviation.

3.4 Relationship of Thorium and Free Acid Concentration

The analytical data for all equilibrations of the study are summarized in Tables 4 through 6. These tables present the equilibrium aqueous and organic concentrations of thorium and free acid, the density measurements, and the distribution coefficients calculated from the data. In this discussion, free acid is defined as the amount of acid which would remain if the hydrolyzable ions were removed from the solution; therefore, it is the acid content free of the influence of the hydrolytic character of the thorium. The distribution coefficients of thorium and free acid are calculated as the equilibrium molar ratios of concentration in the organic phase to concentration in the aqueous phase. All experiments were performed starting with equal volumes, 15 ml each, of aqueous solution and TBP-NDD. Also, only the results of the work at 40°C are discussed and presented in detail; however, these results are representative of those at 30 and 60°C.

At 40°C with constant free acid in the system (i.e., when the sum of free acid in the aqueous phase plus free acid in the organic phase was constant), it was shown that as the equilibrium thorium concentration in the aqueous phase is increased, the equilibrium concentration of thorium in the organic phase increases. When total thorium in the system (thorium in the aqueous plus thorium in the organic phase) is constant, and equilibrium free acid is increased in the aqueous phase, equilibrium thorium in the organic phase increases (see Fig. 1) and thorium in the aqueous phase decreases (see Fig. 2). These changes in equilibrium concentration apply to both the two- and the three-phase regions, which are defined by the incipient three-phase (ITP) boundary curve.

Figure 3 shows the thorium-free acid relationship in another way. As thorium in the system is increased (i.e., in the case of starting solution sets A through G), the equilibrium

Table 4 Equilibration of thorium nitrate-nitric acid solutions with 30% TBP NDD at 30°C

Initial solution concentration		Equilibration volume		Aqueous phase			Organic phase			Distribution coefficient	
Thorium (*M*)	Free acid (*M*)	Organic (ml)	Aqueous (ml)	Thorium (*M*)	Free acid (*M*)	Density (g/ml)	Thorium (*M*)	Free acid (*M*)	Density (g/ml)	Thorium	Free acid
0.0500	0.000	15	15	0.0496	0.0000	1.0162	0.0003	0.0004	0.8076	0.0060	
0.0500	0.100	15	15	0.0490	0.0931	1.0187	0.0014	0.0081	0.8081	0.0286	0.0870
0.0500	0.500	15	15	0.0420	0.429	[a]	0.0080	0.066	0.8125	0.1905	0.1538
0.0500	1.000	15	15	0.0336	0.841	1.0366	0.0167	0.167	0.8185	0.4970	0.1986
0.0500	3.000	15	15	0.0160	2.538	1.0840	0.0320	0.497	0.8342	2.000	0.1958
0.100	0.0500	15	15	0.0944	0.0449	1.0360	0.0052	0.0054	0.8094	0.0551	0.1203
0.100	1.500	15	15	0.0544	1.268	1.0590	0.0449	0.236	0.8316	0.8254	0.1861
0.200	0.000	15	15	0.173	0.0003[b]	1.0677	0.0239	0.0016	0.8164	0.1382	
0.200	0.100	15	15	0.166	0.0863	1.0677	0.0308	0.0142	0.8192	0.1855	0.1645
0.200	0.500	15	15	0.148	0.424	1.0701	0.0517	0.0771	0.8289	0.3493	0.1818
0.200	0.996	15	15	0.128	0.846	1.0754	0.0700	0.148	0.8385	0.5469	0.1749
0.200	2.991	15	15	0.0872	2.604	1.1145	0.1074	0.395	0.8609	1.2317	0.1517
0.300	0.250	15	15	0.222	0.214	1.0951	0.0706	0.0378	0.8360	0.3180	0.1766
0.500	0.000	15	15	0.383	0.0060[b]	1.1472	0.123	0.0016	0.8550	0.3211	
0.500	0.100	15	15	0.369	0.0869	1.1475	0.133	0.0149	0.8580	0.3604	0.1715
0.500	0.500	15	15	0.351	0.431	1.1512	0.150	0.068	0.8661	0.4274	0.1578
0.500	1.000	15	15	0.322	0.864	1.1579	0.161	0.127	0.8743	0.5000	0.1470
0.500	3.000	15	15	0.287	2.728	1.1974	0.217	0.312	[c]	0.7561	0.1144
0.750	0.750	15	15	0.534	0.671	1.2278	0.234	0.104	[c]	0.4382	0.1550
0.999	0.000	15	15	0.750	0.0092[b]	1.2919	0.276	0.0057	[c]	0.3680	
1.000	0.100	15	15	0.658	0.0851	1.2940	0.263	0.0135	[c]	0.3997	0.1586
1.000	0.500	15	15	0.680	0.451	1.3016	0.285	0.0618	[c]	0.4191	0.1370
1.000	1.000	15	15	0.737	0.910	1.3126	0.299	0.113	[c]	0.4057	0.1242
1.000	3.001	15	15	0.729	2.844	1.3643	0.314	0.238	[c]	0.4307	0.0837
1.250	0.0500	15	15	0.958	0.0321	1.3751	0.320	0.0079	[c]	0.3340	0.2469
1.250	1.500	15	15	0.951	1.416	1.4126	0.317	0.147	[c]	0.3333	0.1038
1.499	0.000	15	15	1.199	0.0137[b]	1.4623	0.336	0.0049	[c]	0.2802	
1.500	0.500	15	15	1.208	0.504	1.4753	0.340	0.045	[c]	0.2815	0.0893
1.500	3.000	15	15	1.197	2.920	1.5420	0.358	0.191	[c]	0.2991	0.0654
0.500	3.000	24.3	15[d]	0.211	2.443	1.1623	0.194	0.314	0.882	0.919	0.129
0.750	0.750	20.2	15.2[d]	0.475	0.623	1.2083	0.208	0.0891	0.889	0.438	0.143
0.999	0.000	26.0	15.1[d]	0.624	0.0131[b]	1.2461	0.226	0.0035	0.891	0.362	
1.000	0.100	28.2	15.1[d]	0.596	0.0797	1.2391	0.223	0.0118	0.892	0.374	0.168
1.000	0.500	34.2	15.1[d]	0.532	0.380	1.2215	0.216	0.0539	0.889	0.406	0.142
1.000	1.000	41.4	15.2[d]	0.453	0.743	1.2030	0.208	0.1018	0.890	0.459	0.137
1.250	0.0500	45.2	15.2[d]	0.613	0.0272	1.2421	0.224	0.0061	0.884	0.365	0.224
1.250	1.500	43.6	10.1[d]	0.409	1.007	1.190	0.201	0.134	0.888	0.491	0.133

[a] Not analyzed

[b] Negative free acid indicates the acid deficient condition

[c] Three phases were present after equilibration

[d] Incipient three phase experiments Two phases were present after equilibration The addition of a small amount of aqueous $Th(NO_3)_4$ HNO_3 causes three phases to form

thorium concentration increases in both aqueous and organic phases. The increase in thorium concentration in the system also produces a change in the free acid distribution between phases. As the thorium is increased, the equilibrium free acid increases in the aqueous phase and decreases in the organic phase (Fig. 4). When no free acid was initially added to the thorium nitrate, after equilibration, the aqueous phase became acid deficient because of the hydrolysis of thorium to liberate acid and the resulting transfer of the acid into the organic phase. The increase in acid deficiency was observed with an increase in thorium concentration, except in the case of ITP experiments (Tables 4–6).

A related effect is produced by changing the free acid in a system in which the thorium remains constant. At constant thorium (e.g., solution set E, Table 1), an increase in the free acid at equilibrium causes the thorium concentration to increase in the organic phase and to decrease in the aqueous phase (Fig. 3).

Table 5 Equilibration of thorium nitrate nitric acid solutions in 30% TBP NDD at 40°C

Initial solution concentration		Equilibration volume		Aqueous phase			Organic phase			Distribution coefficient	
Thorium (M)	Free acid (M)	Organic (ml)	Aqueous (ml)	Thorium (M)	Free acid (M)	Density (g/ml)	Thorium (M)	Free acid (M)	Density (g/ml)	Thorium	Free acid
0.0500	0.000	15	15	0.0496	0.0006	1.0123	0.00066	0.0006	0.7996	0.013	1.000
0.0500	0.100	15	15	0.0491	0.0955	1.0149	0.00133	0.00682	0.8002	0.027	0.0714
0.0500	0.500	15	15	0.0431	0.438	1.0235	0.00710	0.0597	0.8040	0.1647	0.1363
0.0500	1.000	15	15	0.0347	0.844	1.0332	0.0155	0.1452	0.8098	0.4467	0.1720
0.0500	3.000	15	15	0.0177	2.483	1.0789	0.322	0.489	0.8257	1.8192	0.1969
0.1000	0.050	15	15	0.0950	0.0458	1.0326	0.00440	0.00439	0.8012	0.0463	0.0959
0.100	1.500	15	15	0.0575	1.256	1.0554	0.0431	0.229	0.8226	0.7496	0.1823
0.200	0.000	15	15	0.181	0.00135[a]	1.0653	0.0200	0.00159	0.8069	0.1105	
0.200	0.100	15	15	0.174	0.0885	1.0656	0.0263	0.01264	0.8097	0.1511	0.1428
0.200	0.500	15	15	0.155	0.427	1.0679	0.0473	0.0708	0.8192	0.3052	0.1658
0.200	0.996	15	15	0.134	0.845	1.0726	0.0670	0.1434	0.8289	0.5000	0.1697
0.200	2.991	15	15	0.0921	2.580	1.1106	0.1065	0.414	0.8512	1.1564	0.1605
0.300	0.250	15	15	0.238	0.215	1.0934	0.0670	0.0357	0.8257	0.2815	0.1660
0.500	0.000	15	15	0.388	0.00574[a]	1.1461	0.124	0.00266	0.8438	0.3196	
0.500	0.100	15	15	0.384	0.0792	1.1461	0.130	0.01314	0.8474	0.3385	0.1659
0.500	0.500	15	15	0.365	0.422	1.1487	0.147	0.0670	0.8557	0.4027	0.1588
0.500	1.000	15	15	0.349	0.854	1.1551	0.166	0.1290	0.8639	0.4756	0.1511
0.500	3.000	15	15	0.312	2.648	1.1968	0.203	0.318	0.898	0.6506	0.1201
0.750	0.750	15	15	0.547	0.642	1.2268	0.212	0.0888	0.8829	0.3876	0.1383
0.999	0.000	15[b]	15	0.763	0.0130[a]	1.2908	0.251	0.00580	0.8472	0.3290	
1.000	0.100	15[b]	15	0.759	0.0827	1.2923	0.258	0.01384	0.8486	0.3399	0.1674
1.000	0.500	15[b]	15	0.746	0.437	1.2988	0.267	0.0586	0.8509	0.3579	0.1341
1.000	1.000	15[b]	15	0.741	0.895	1.3091	0.277	0.1078	0.8531	0.3738	0.1204
1.000	3.001	15[b]	15	0.728	2.752	1.3590	0.289	0.246	0.8581	0.3970	0.0894
1.250	0.050	15[b]	15	0.979	0.0349	1.3706	0.308	0.00822	0.8573	0.3146	0.2355
1.250	1.500	15[b]	15	0.979	1.393	1.4064	0.315	0.1304	0.8610	0.3218	0.0936
0.999	0.000	20.9	18.6[c]	0.761	0.0136[a]	1.2862	0.2552	0.00439	0.892	0.3768	
1.000	0.100	18.3	15.1[c]	0.738	0.0769	1.2787	0.2549	0.0126	0.892	0.4186	0.1986
1.000	0.500	23.0	15.1[c]	0.600	0.418	1.2635	0.2412	0.0575	0.890	0.365	0.138
1.000	1.000	28.7	15.05[c]	0.598	0.815	1.2471	0.2373	0.1075	0.890	0.897	0.132
1.000	3.001	37.4	12.1[c]	0.383	2.275	1.2104	0.2153	0.282	0.886	0.162	0.124
1.250	0.0500	33.9	15.2[c]	0.751	0.0280	1.2827	0.2546	0.00697	0.894	0.339	0.249
1.250	1.5000	43.2	13.1[c]	0.553	1.085	1.2369	0.2318	0.1395	0.889	0.419	0.129

[a] Negative free acid indicates the acid deficient condition.

[b] Three phases were present after equilibration. The organic phase density represents organic phase diluted with an equal volume of 30% TBP NDD.

[c] Incipient three phase experiments. Two phases were present after equilibration. The addition of a small amount of aqueous $Th(NO_3)_4$ HNO_3 causes three phases to form.

Thorium and free acid are therefore shown to be interactive in final equilibrium concentrations for both aqueous and organic phases. Changes in the thorium concentration in the system result in predictable changes in the free acid equilibrium between the phases. Data plots with these characteristics produce families of curves typical of the data presented in Fig. 4.

Thorium concentrations related to free acid changes in the region of the incipient third-phase (ITP) boundary condition exhibit different slope characteristics than those presented in the clearly defined two- and three-phase regions. These equilibrium concentration changes are characterized by decreases in allowable thorium concentration in both aqueous and organic phases as the system free acid is increased. The condition is shown in Figs. 1 and 2. The data set indicated for the ITP line defines the boundary condition. The transition to the three-phase system occurs at concentrations above the limits imposed by these conditions.

It is believed that the single organic-phase solubility limit of the thorium nitrate-TBP complex is 30% TBP at 30, 40 and 60°C was measured by the ITP measurements. The equilibrium boundary limits for free acid and thorium concentration for the two- and three-phase regions are shown in Fig. 5 for 30, 40, and 60°C.

Table 6 Equilibration of thorium nitrate nitric acid solutions in 30% TBP NDD at 60°C

Initial solution concentration		Equilibration volume		Aqueous phase			Organic phase			Distribution coefficient	
Thorium (*M*)	Free acid (*M*)	Organic (ml)	Aqueous (ml)	Thorium (*M*)	Free acid (*M*)	Density (g/ml)	Thorium (*M*)	Free acid (*M*)	Density (g/ml)	Thorium	Free acid
0 0500	0 000	15	15	0 0499	0 00093	1 0030	0 00061	0 00057	0 7838	0 0122	0 6129
0 0500	0 100	15	15	0 0494	0 0981	1 0055	0 00113	0 00558	0 7842	0 0229	0 0569
0 0500	0 500	15	15	0 0443	0 451	1 0145	0 00603	0 0523	0 7873	0 1361	0 1160
0 0500	1 000	15	15	0 0368	0 866	1 0241	0 0137	0 138	0 7928	0 3723	0 1594
0 0500	3 000	15	15	0 0202	2 516	1 0676	0 0293	0 525	0 8087	1 4505	0 2087
0 100	0 0500	15	15	0 0970	0 0475	1 0233	0 00334	0 00357	0 7852	0 0344	0 0752
0 100	1 500	15	15	0 0615	1 265	1 0463	0 0392	0 230	0 8047	0 6374	0 1818
0 200	0 000	15	15	0 188	0 00176^{a}	1 0570	0 0150	0 00238	0 7892	0 0798	
0 200	0 100	15	15	0 183	0 0912	1 0573	0 0212	0 0113	0 7918	0 1158	0 1239
0 200	0 500	15	15	0 163	0 431	1 0600	0 0410	0 0654	0 8005	0 2515	0 1517
0 200	0 996	15	15	0 142	0 852	1 0645	0 0605	0 139	0 8102	0 4260	0 1631
0 200	2 991	15	15	0 103	2 564	1 1009	0 0980	0 427	0 8319	0 9515	0 1665
0 300	0 250	15	15	0 248	0 217	1 0863	0 0580	0 0332	0 8060	0 2339	0 1530
0 500	0 000	15	15	0 405	0 0066^{a}	1 1399	0 1055	0 00483	0 8224	0 2605	
0 500	0 100	15	15	0 395	0 0843	1 1396	0 1145	0 0156	0 8261	0 2899	0 1851
0 500	0 500	15	15	0 377	0 434	1 1413	0 134	0 0710	0 8350	0 3554	0 1636
0 500	1 000	15	15	0 358	0 868	1 1468	0 153	0 137	0 8438	0 4274	0 1578
0 500	3 000	15	15	0 325	2 656	1 1874	0 180	0 366	0 8606	0 5538	0 1378
0 750	0 750	15	15	0 551	0 654	1 2170	0 206	0 0966	0 8626	0 3739	0 1477
0 999	0 000	15	15	0 775	0 0127^{a}	1 2825	0 241	0 0068	0 8726	0 3110	
1 000	0 100	15	15	0 764	0 0750	1 2838	0 246	0 0152	0 8757	0 3220	0 2027
1 000	0 500	15	15	0 755	0 429	1 2907	0 253	0 0651	0 8809	0 3351	0 1517
1 000	1 000	15	15	0 748	0 871	1 3014	0 258	0 125	0 8875	0 3449	0 1435
1 000	3 001	15	15	0 751	2 692	1 3486	0 290	0 299	0 8378	0 3862	0 1111
1 250	0 0500	15	15	0 979	0 0310	1 3616	0 290	0 0123	0 8377	0 2962	0 3968
1 250	1 500	15	15	0 978	1 362	1 3944	0 302	0 167	0 8419	0 3088	0 1226
1 499	0 000	15	15	1 206	0 0156^{a}	1 4429	0 331	0 0104	0 8454	0 2745	
1 500	0 0999	15	15	1 210	0 0827	1 4437	0 333	0 0158	0 8459^{b}	0 2752	0 1911
1 500	0 500	15	15	1 209	0 448	1 4535	0 333	0 0581	0 8466^{b}	0 2754	0 1297
1 500	1 000	15	15	1 213	0 925	1 4669	0 325	0 108	0 8469^{b}	0 2679	0 1168
1 000	3 001	27 1	15 3	0 624	2 654	1 2978	0 235	0 314	0 880	0 377	0 118
1 250	0 0500	17 7	15 5	0 966	0 0332	1 3541	0 278	0 0112	0 889	0 288	0 337
1 250	1 500	30 8	15 3	0 776	1 255	1 3201	0 257	0 163	0 884	0 331	0 130
1 499	0 000	31 4	15 1	0 970	0 0089^{a}	1 3619	0 278	0 0083	0 886	0 287	
1 500	0 0999	27 9	13 1	0 948	0 0681	1 3542	0 281	0 0145	0 889	0 296	0 213
1 500	0 500	25 8	13 1	0 901	0 388	1 3430	0 275	0 0565	0 886	0 305	0 146
1 500	1 000	35 4	13 3	0 845	0 778	1 3333	0 270	0 108	0 884	0 320	0 139

[a] Negative free acid indicates the acid deficient condition

[b] Three phases were present after equilibration The organic phase density represents organic phase diluted with an equal volume of 30% TBP NDD

3.5 Relationship of Thorium, Free Acid, and Temperature

The thorium and free acid relationship exhibited by the ITP data is consistent with the results of earlier studies of the solvent extraction of thorium with TBP. It has been shown by McKay et al. and by Schulz[5] that the solubility of the thorium nitrate-TBP complex (as a single-phase organic entity) decreases with the increase in nitric acid concentration of the organic phase; at constant nitric acid concentration in the organic phase, solubility of thorium increases with increase in temperature.

The plot of data (Fig. 5), which shows changes in the boundaries between the two- and three-phase regions, corresponds to the earlier work and shows that a constant temperature, the solubility of thorium in the organic layer decreases with an increase of free acid in the system. A corresponding relationship is true for the aqueous layer. At a constant temperature with an increase of free acid in the system, the limit for thorium in the two-phase region is decreased. Also, as temperature is increased, overall solubility of thorium nitrate in the TBP-NDD system is increased, which indicates that a family of curves (which show

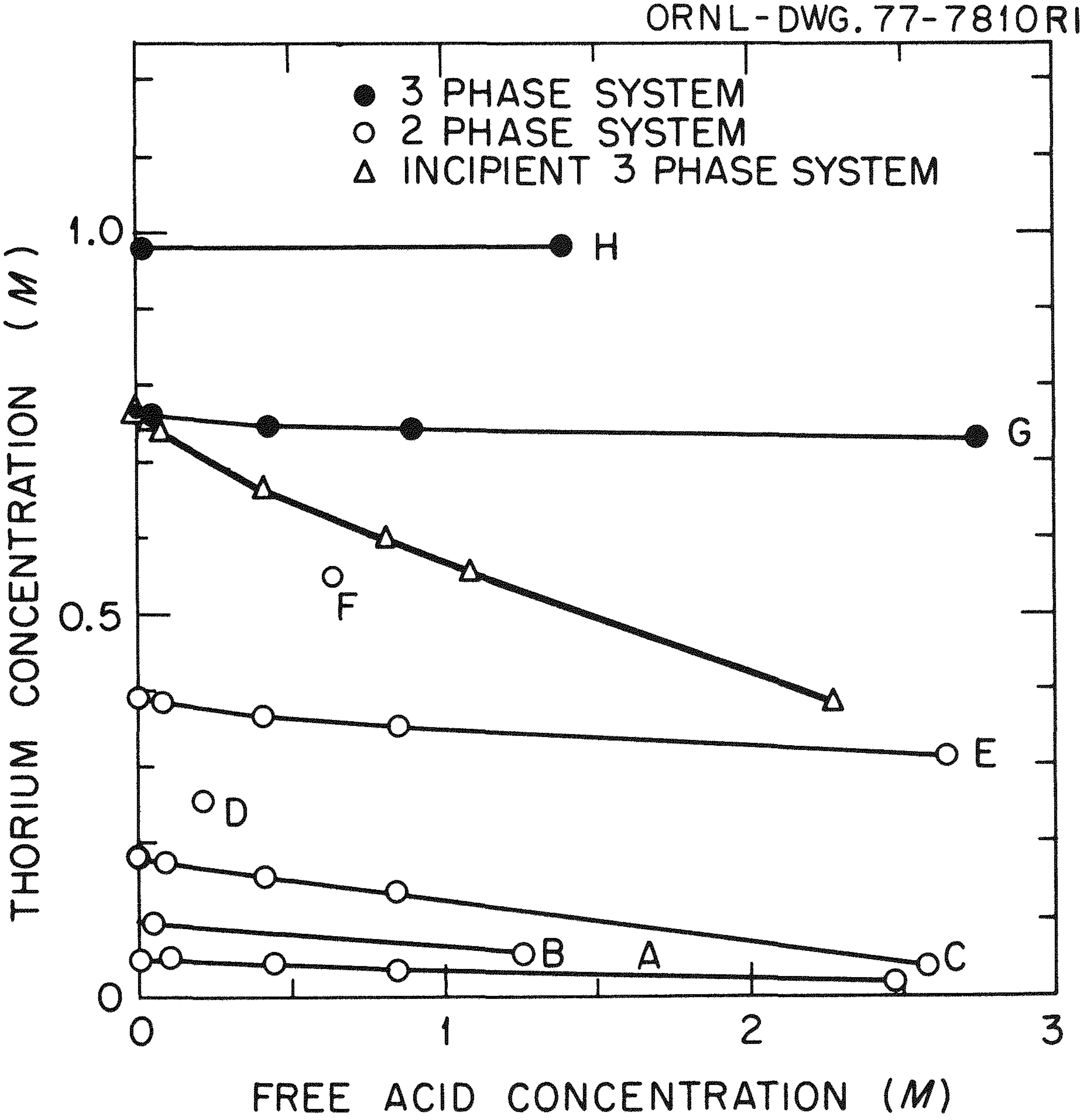

Fig. 1. **Aqueous-phase thorium concentration response to free acid concentration change at 40°C.** (Initial aqueous thorium concentrations: A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.0 *M*; H, 1.25 *M*; initial free acid concentrations: 0–3.0 *M*).

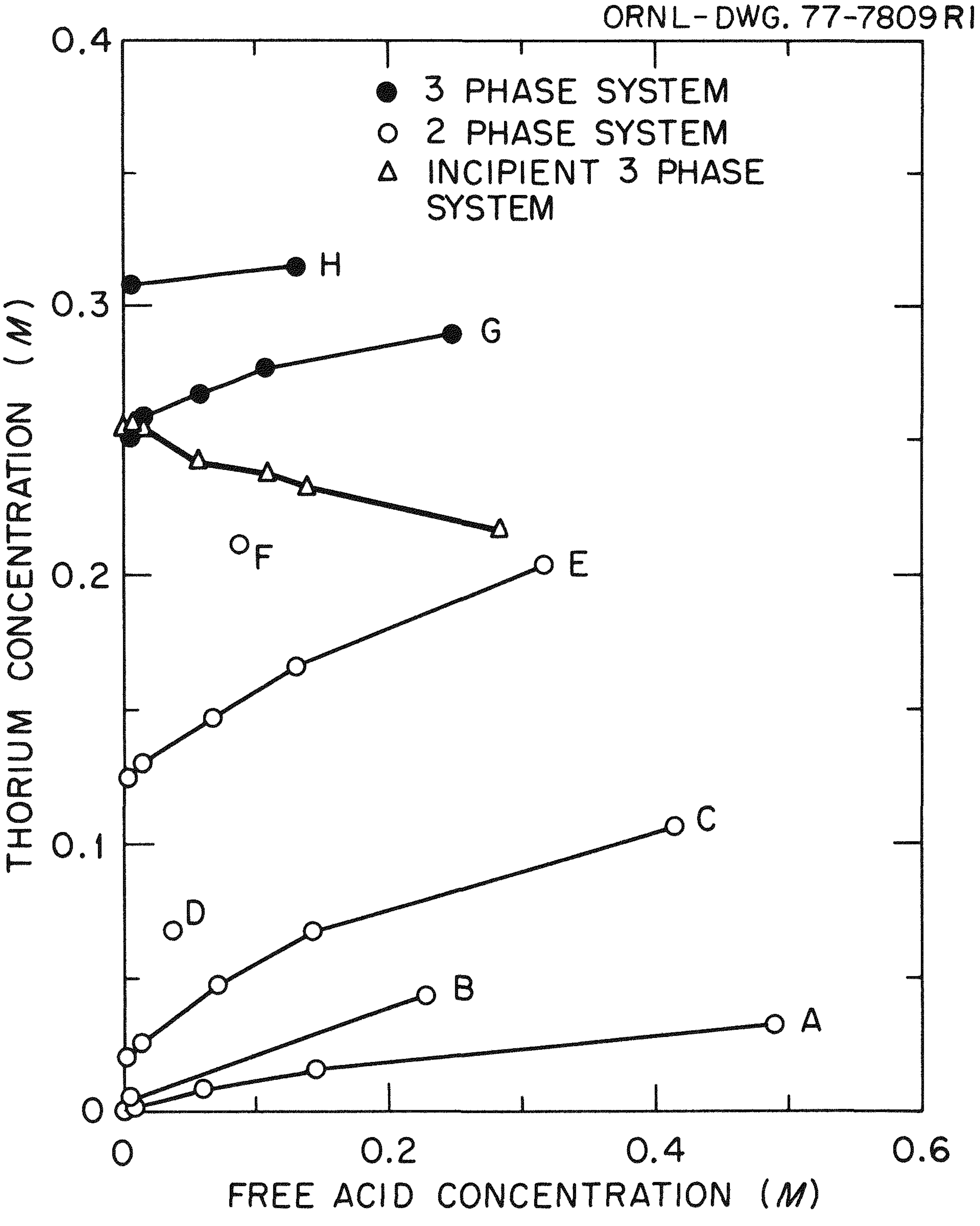

Fig. 2. Organic-phase thorium concentration response to free acid concentration change at 40°C. (Initial aqueous thorium concentrations: A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.0 *M*; H, 1.25 *M*; initial aqueous free acid concentrations: 0–3.0 *M*).

ORNL-DWG. 77-7811R1

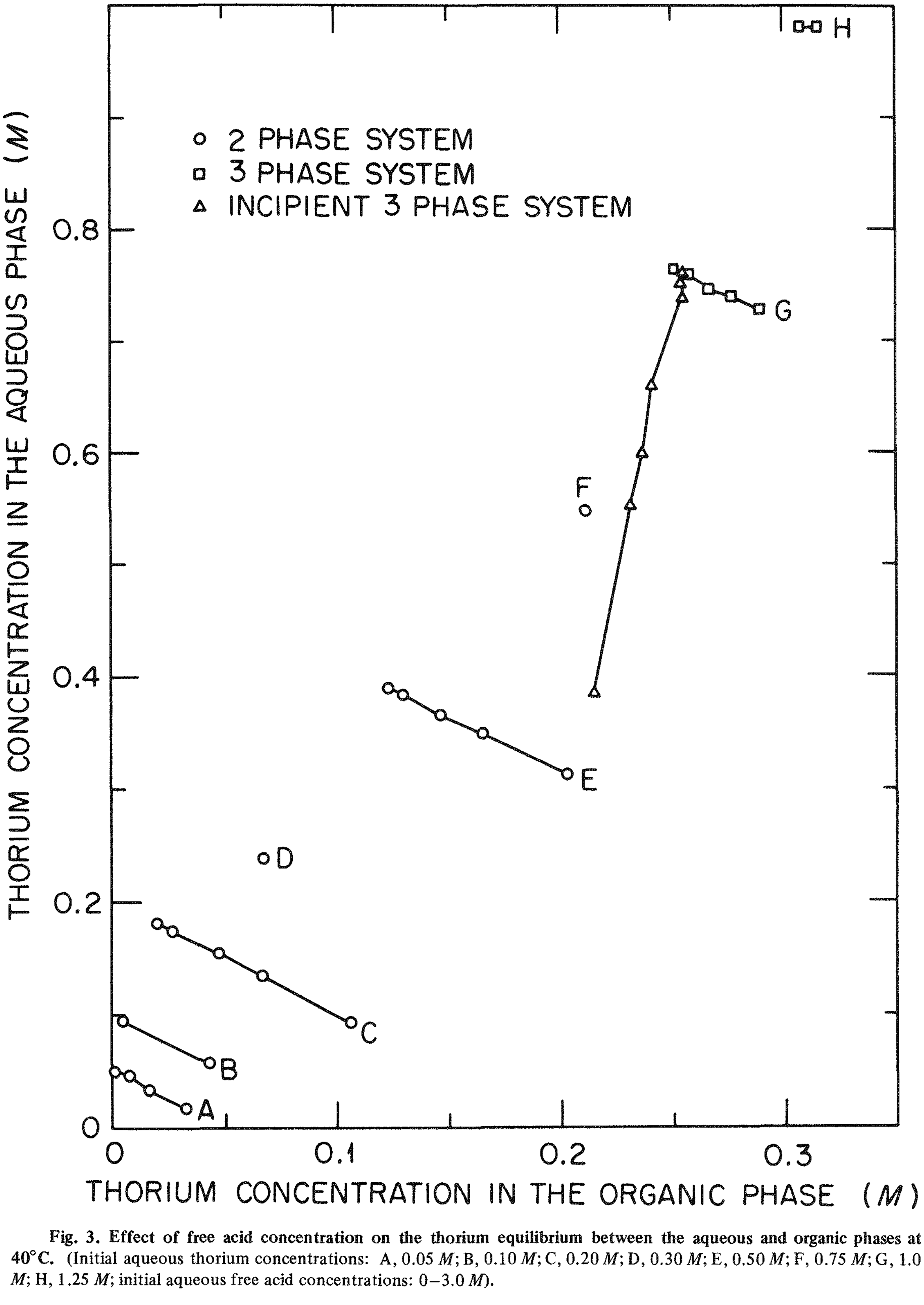

Fig. 3. Effect of free acid concentration on the thorium equilibrium between the aqueous and organic phases at 40°C. (Initial aqueous thorium concentrations: A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.0 *M*; H, 1.25 *M*; initial aqueous free acid concentrations: 0–3.0 *M*).

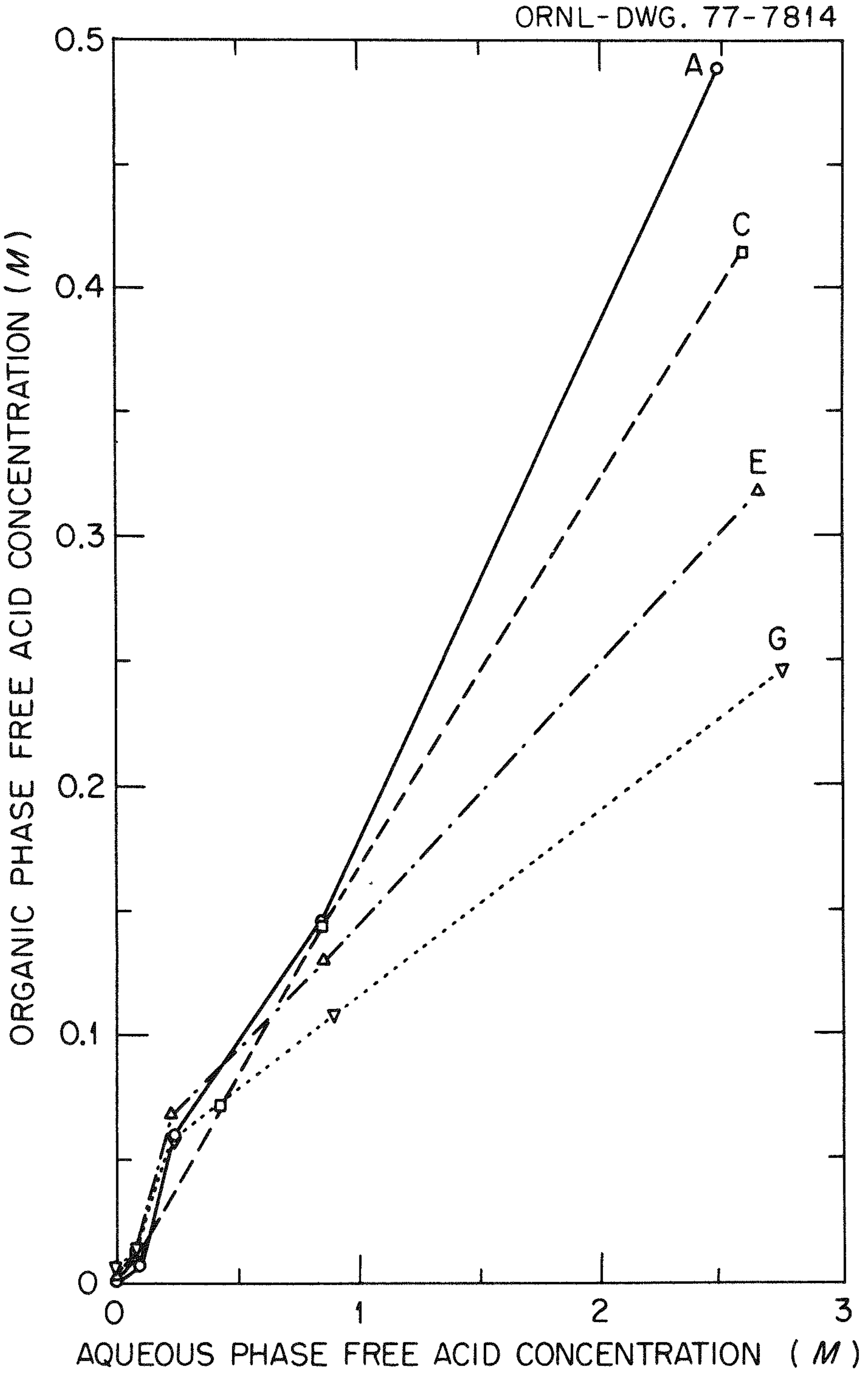

Fig. 4. Typical plot of equilibrium of free acid between aqueous and organic phases showing influence of thorium concentration at 40°C. (Initial aqueous thorium concentrations: A, 0.05 *M*; C, 0.20 *M*; E, 0.50 *M*; G, 1.0 *M*; initial aqueous free acid concentrations: 0–3.0 *M*).

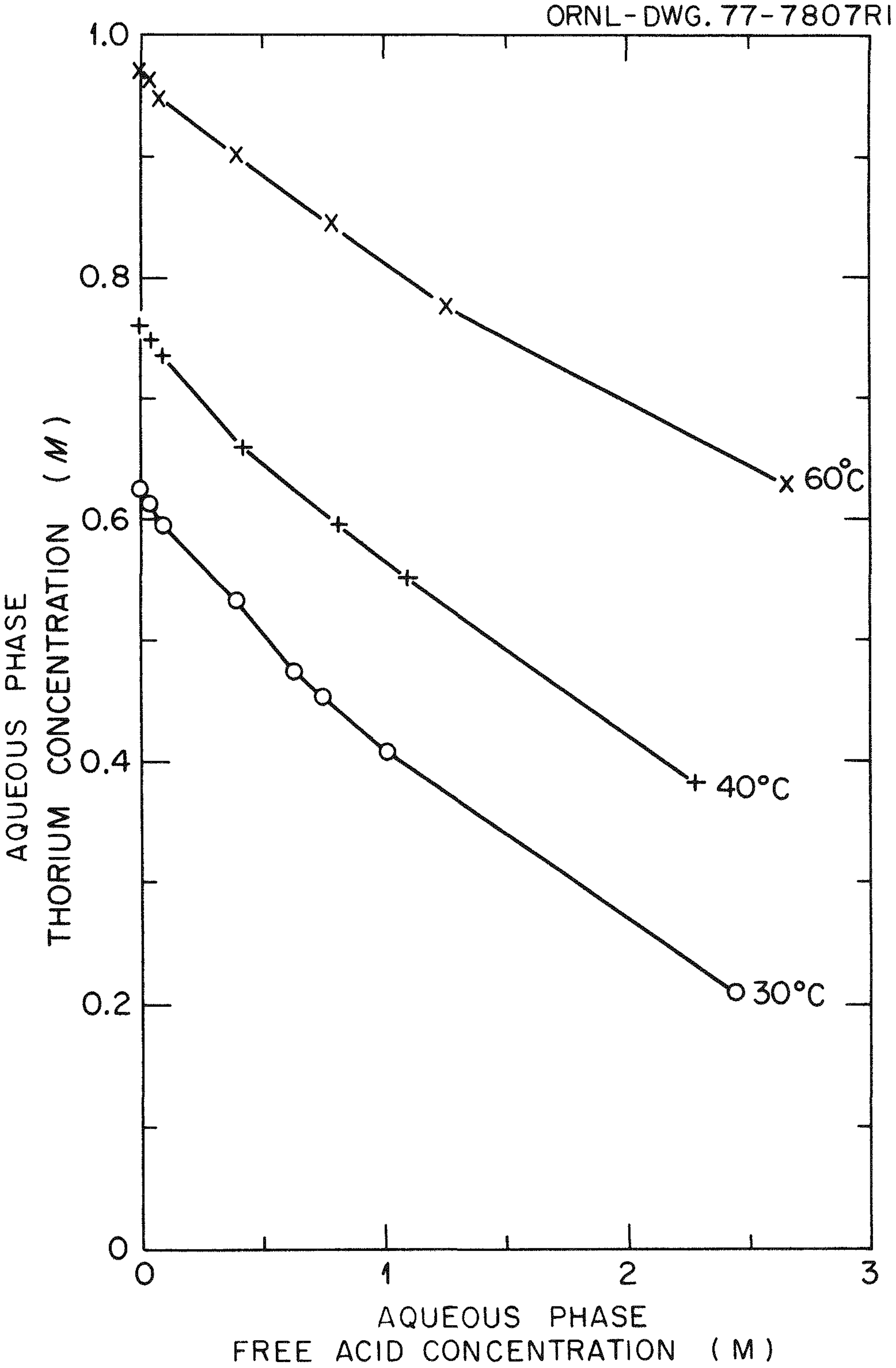

Fig. 5. Aqueous phase limiting conditions for two- and three-phase boundary regions. For each temperature, three phases are above the boundary and two phases are below.

the limits of thorium-to-free acid concentration for any specified temperature) can be constructed. As shown in Figs. 5 and 6, the relationship of phase concentration limits and temperature applies to both aqueous and organic layers. When any two of the three parameters (thorium, free acid, and temperature) are known, the limit of the two-phase region for the third parameter can be determined.

3.6 Relationship of Thorium, Free Acid, and Density

As the concentrations of thorium and free acid are changed, changes also occur in the densities of the phases. As equilibrium thorium is increased by increases in total system concentration (thorium in the aqueous phase plus thorium in the organic phase) and holding free acid constant, the density increases (Fig. 7) for each phase. When thorium is constant in the system (e.g., solution set E, Table 1), as equilibrium free acid increases in the aqueous and organic phases, density increases.

A presentation of thorium concentration vs densities (Fig. 8) also shows the relationship of thorium, free acid, and density. When free acid in the system is constant, and thorium concentration in either phase is increased, both aqueous and organic equilibrium densities increase. When aqueous thorium in the system is constant (e.g., solution set E, Table 1), and free acid of the system is increased, the density of the aqueous phase at equilibrium is decreased and density of the organic phase is increased.

The data of the 30°C test series (shown in Fig. 9) demonstrate the correlation of concentration parameters and density. The equilibrium concentrations of free acid plus thorium of the aqueous and organic phases are plotted vs the densities of the phases. This presentation shows that at equilibrium, as the sum of the concentrations of the two parameters is increased in a phase, the density of the phase is increased.

The data from the studies at 30, 40, and 60°C were plotted to graphically determine the relationships which describe the system equilibria. The equations obtained having greater than 0.99 correlation for each temperature are shown in Table 7. It was determined that the density of the system is a function of thorium concentration (*M*) plus 0.08 times free acid (*M*). An expression which describes the concentration relationships is developed in Appendix A. The coefficient derived, 0.08, is consistent with graphic representation of the data.

Table 7. Equations for experimental data fit of aqueous and organic phases

Phase	Temperature (°C)	Equation[a]
Aqueous	30	$D = 0.3839\,C + 1.0020$
Aqueous	40	$D = 0.3823\,C + 0.9960$
Aqueous	60	$D = 0.3804\,C + 0.9852$
Organic	30	$D = 0.3852\,C + 0.8071$
Organic	40	$D = 0.3774\,C + 0.7991$
Organic	60	$D = 0.3755\,C + 0.7831$

[a] $C = C_{Th} + 0.08\,C_H$, where C_{Th} = concentration of thorium (*M*) and C_H = concentration of free acid (*M*).

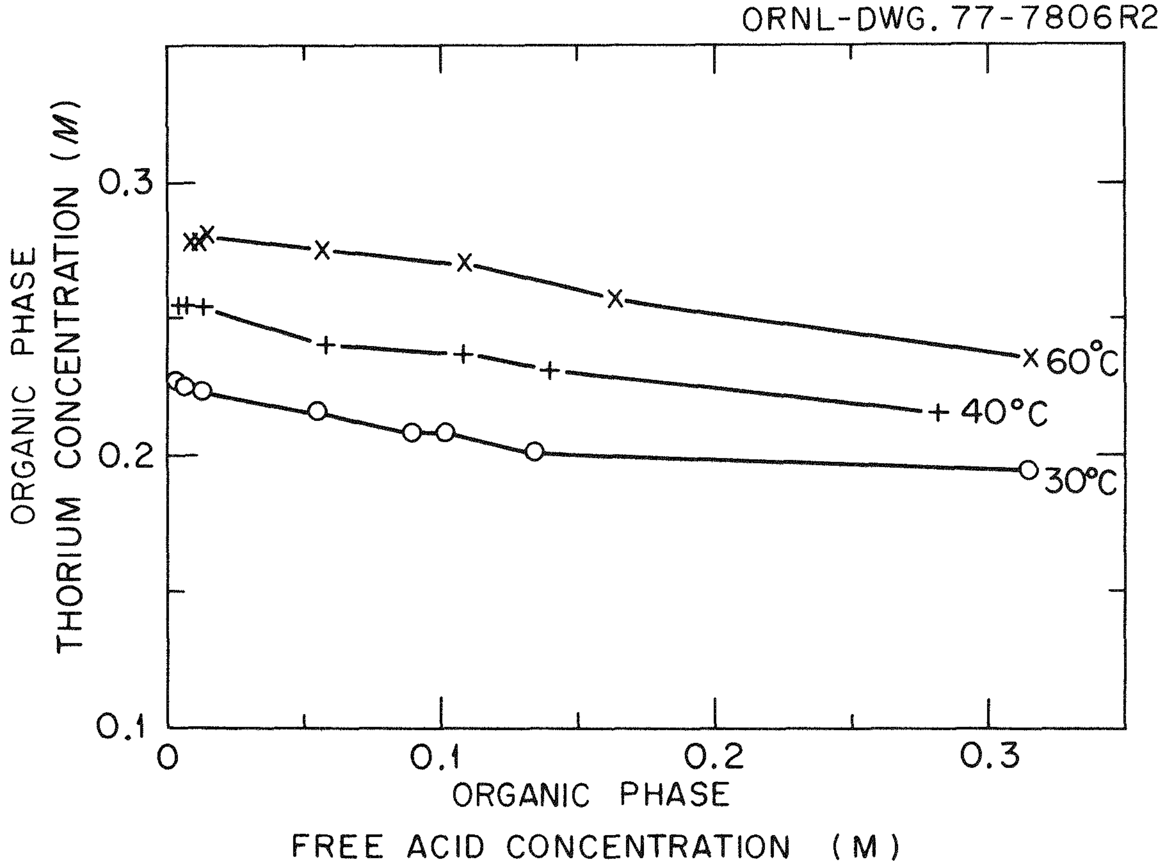

Fig. 6. Organic phase limiting conditions for two- and three-phase boundary regions. For each temperature, three phases are above the boundary and two phases are below.

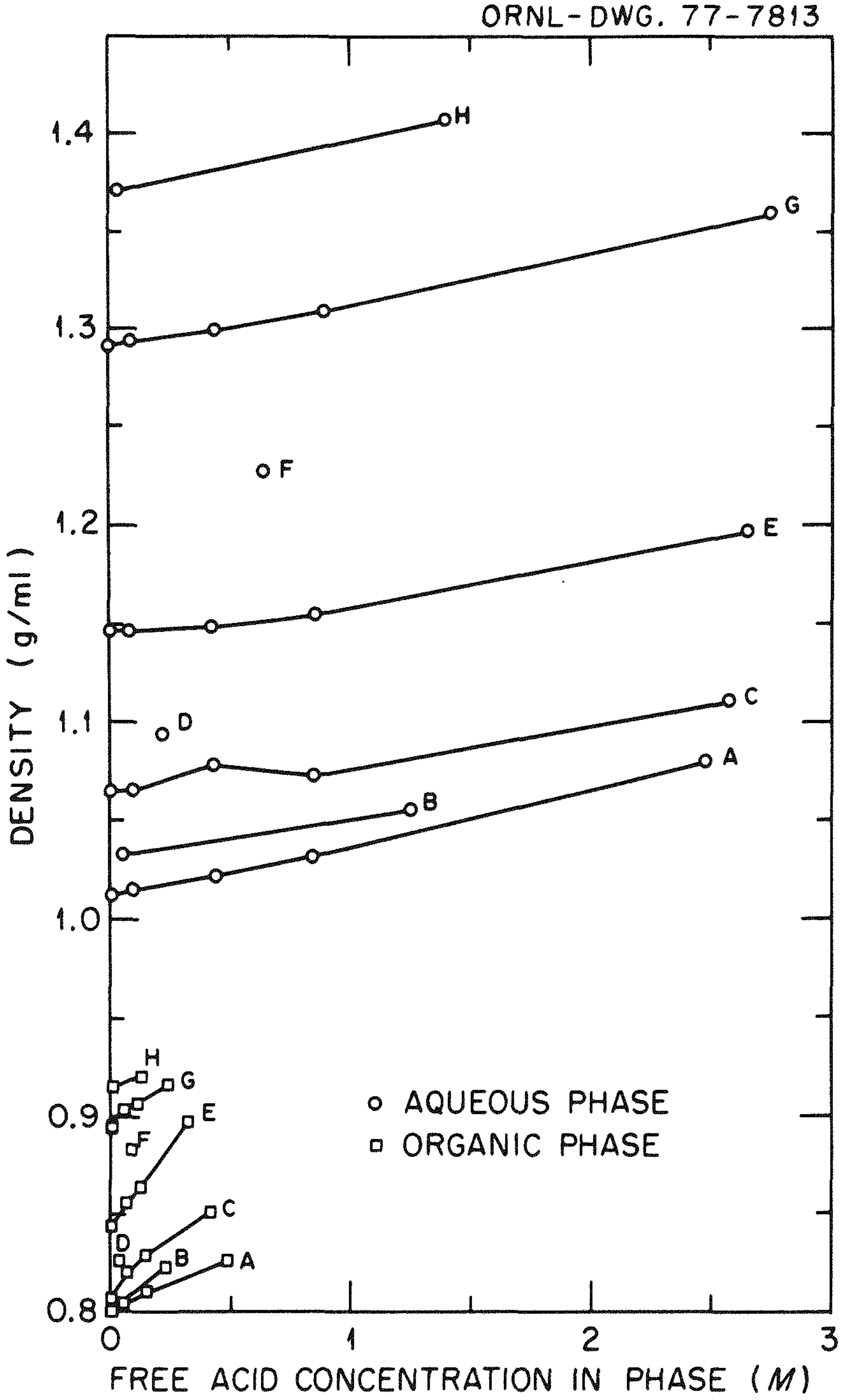

Fig. 7. **Relationship of density of aqueous or organic phase and free acid concentration in the phase at 40°C.** (Initial aqueous thorium concentrations: A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.0 *M*; H, 1.25 *M*; initial aqueous free acid concentrations: 0–3.0 *M*).

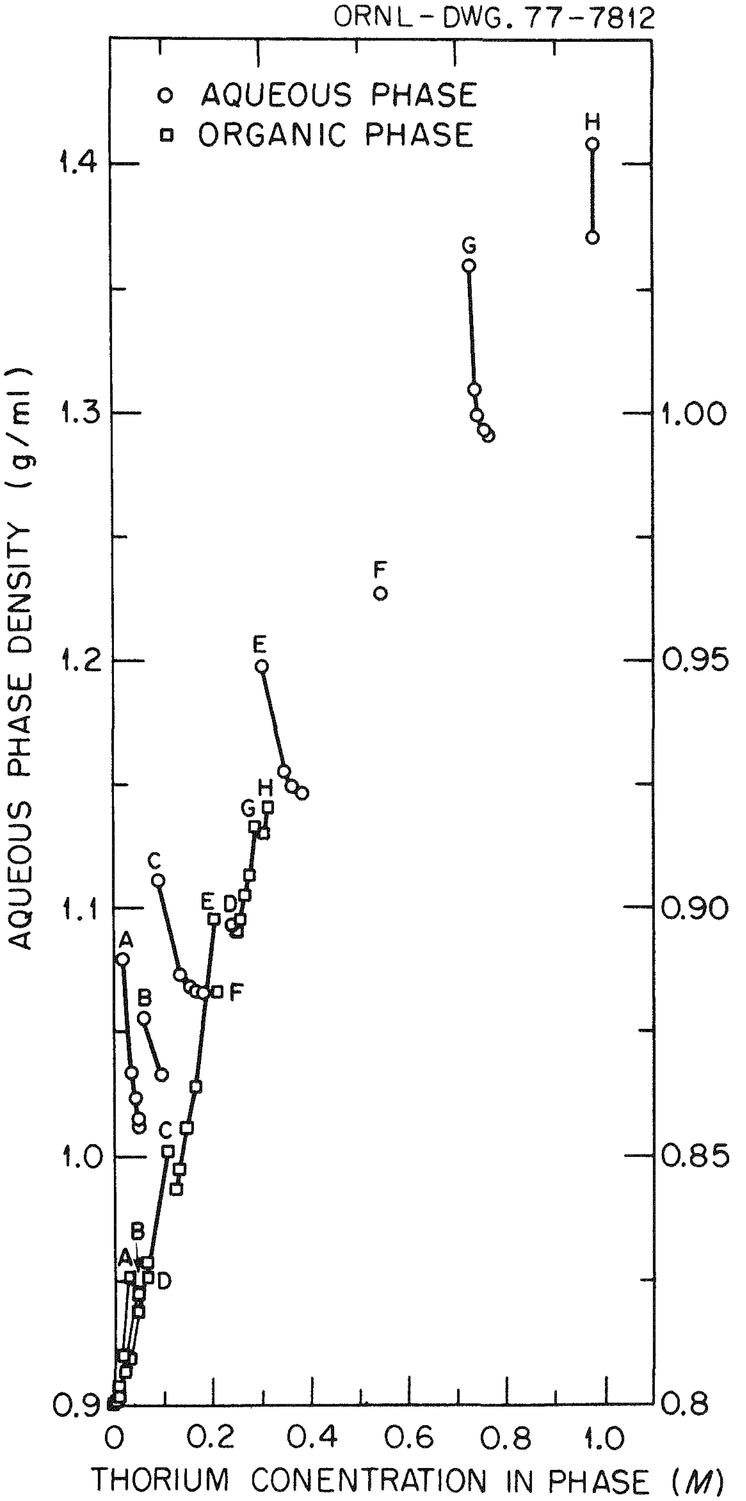

Fig. 8. Relationship of density of aqueous or organic phase and thorium concentration in the phase at 40°C. (Initial aqueous thorium concentrations: A, 0.05 *M*; B, 0.10 *M*; C, 0.20 *M*; D, 0.30 *M*; E, 0.50 *M*; F, 0.75 *M*; G, 1.0 *M*; H, 1.25 *M*; initial aqueous free acid concentrations: 0.30 *M*).

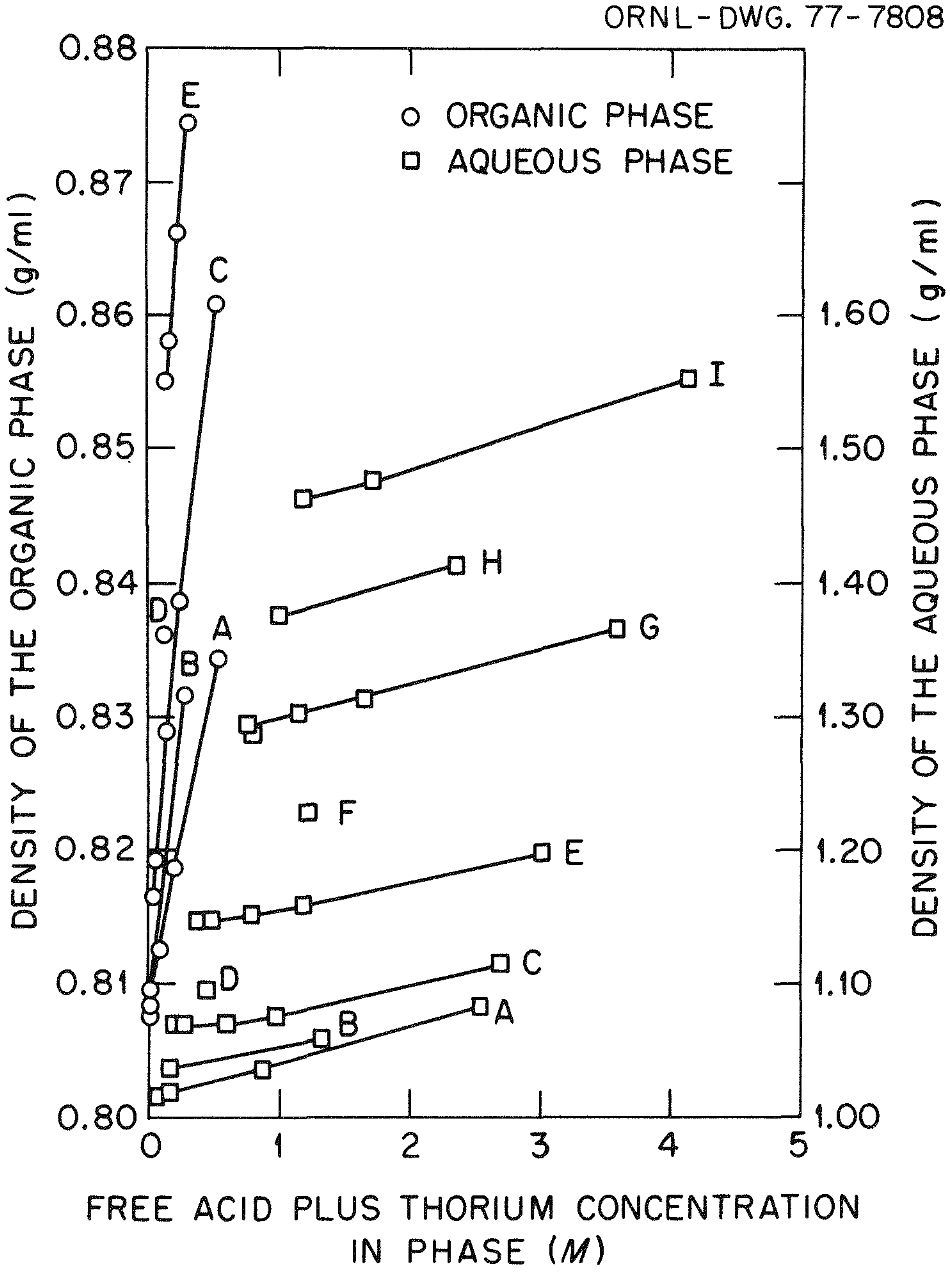

Fig. 9. Relationship of density of aqueous or organic phases and concentration of free acid plus thorium in the phases at 30°C.

The general form of an expression which describes the linear correlation of density (D) of the aqueous or the organic phase of the system is $D = a(C_{Th} + bC_H) + c$, where a is the slope; C_{Th} is the thorium concentration, M; b is the free acid coefficient; C_H is the free acid concentration, M; and c is density intercept, g/ml.

Expanded to include the effect of temperature, the expression is $D = a[(To - Ti)(K_c)(C_{Th} + bC_H)] + e(To - Ti)(K_e)$, where To is the reference temperature, °C; Ti is the system temperature; K_c is the correction constant for thorium and free acid concentration per °C; and K_e is the correction constant for density per °C.

The data from this study are plotted as the relationship of density to thorium nitrate concentration plus (0.08) free acid concentration for the aqueous phases in Figs. 10, 12, and 14 and for the organic phases in Figs. 11, 13, and 15. The temperature correction constants K_c and K_e, which were determined from the equilibration data, are given in Table 8.

Table 8. Temperature corrections for equilibrations at 30, 40, and 60°C

Temperature range (°C)	Phase	K_c	K_e
30–40	Aqueous	0.00015	0.00060
40–60	Aqueous	0.00010	0.00054
30–60	Aqueous	0.00012	0.00056
30–40	Organic	0.00078	0.00080
40–60	Organic	0.00010	0.00080
30–60	Organic	0.00032	0.00080

4. CONCLUSIONS

It has been demonstrated that thorium nitrate concentration, free nitric acid concentration, and density are related in equilibrium behavior between aqueous and organic phases from 30 to 60°C in the TBP-NDD solvent extraction system. Temperature, thorium nitrate, and free acid interact to provide the limiting values which define the boundaries between the two- and three-phase regions. The relationship applies to both aqueous and organic phases.

A linear correlation was observed for the density (D) of the aqueous in the organic phase and the concentration of thorium and free acid. The general form of an expression which decribes the correlation is $D = a(C_{Th} + bC_H) + c$, where a is the slope, C_{Th} and C_H are molar concentrations of thorium and free acid, b is the free acid coefficient, and c is the density intercept.

The data support the mathematical model of the 30% TBP-NDD solvent extraction system and improve the data base for using the SEPHIS-Thorex computer program for solvent extraction system design and simulation.

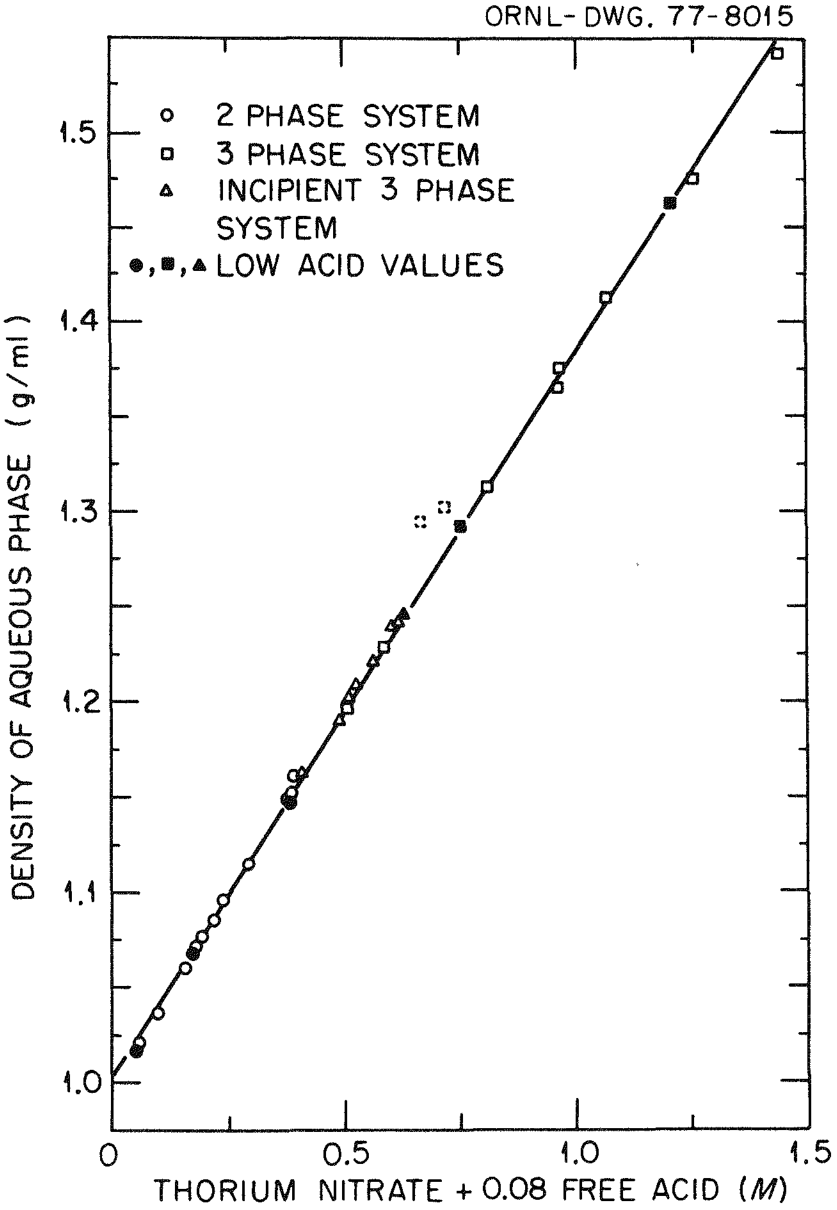

Fig. 10. Relationship of density and thorium nitrate plus free acid for the aqueous phase at 30°C.

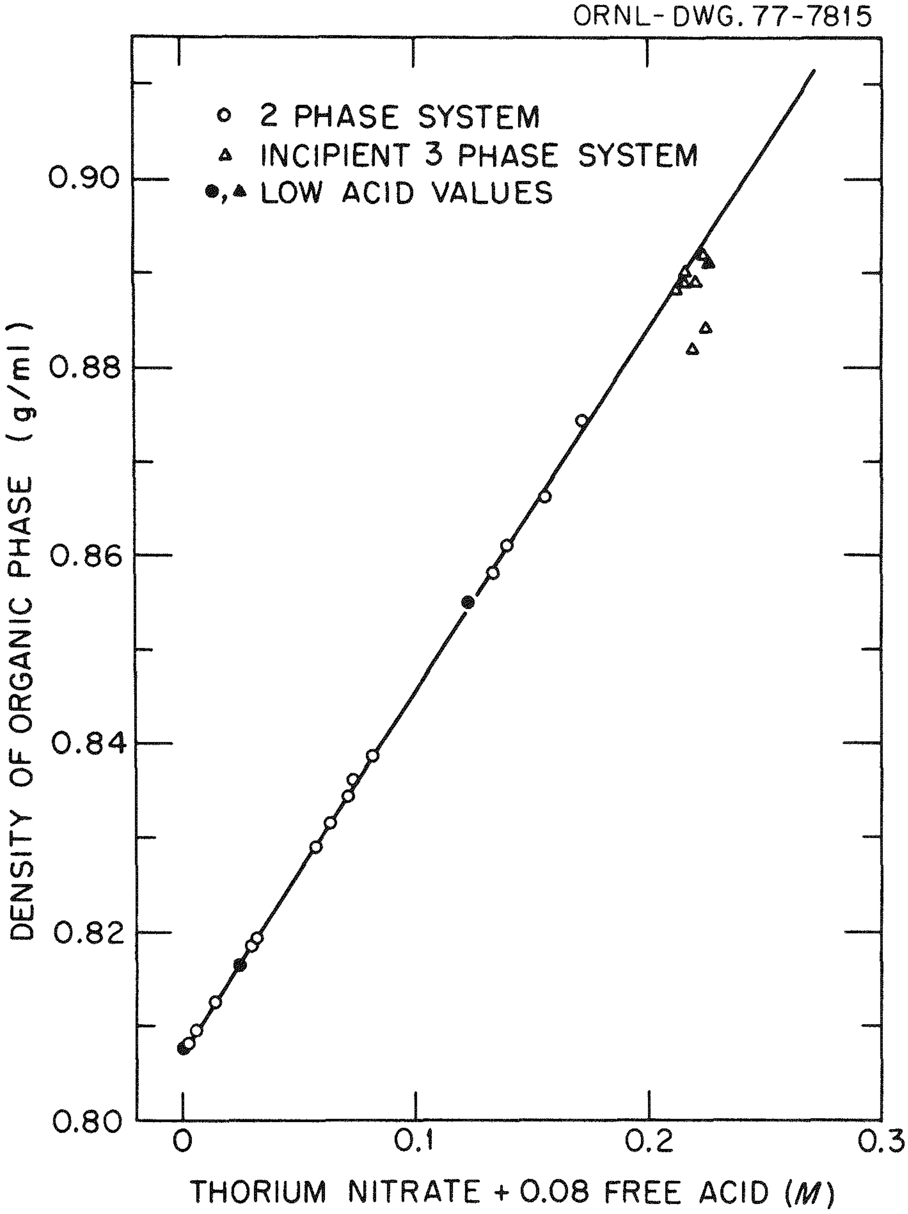

Fig. 11. Relationship of density and thorium nitrate plus free acid for the organic phase at 30°C.

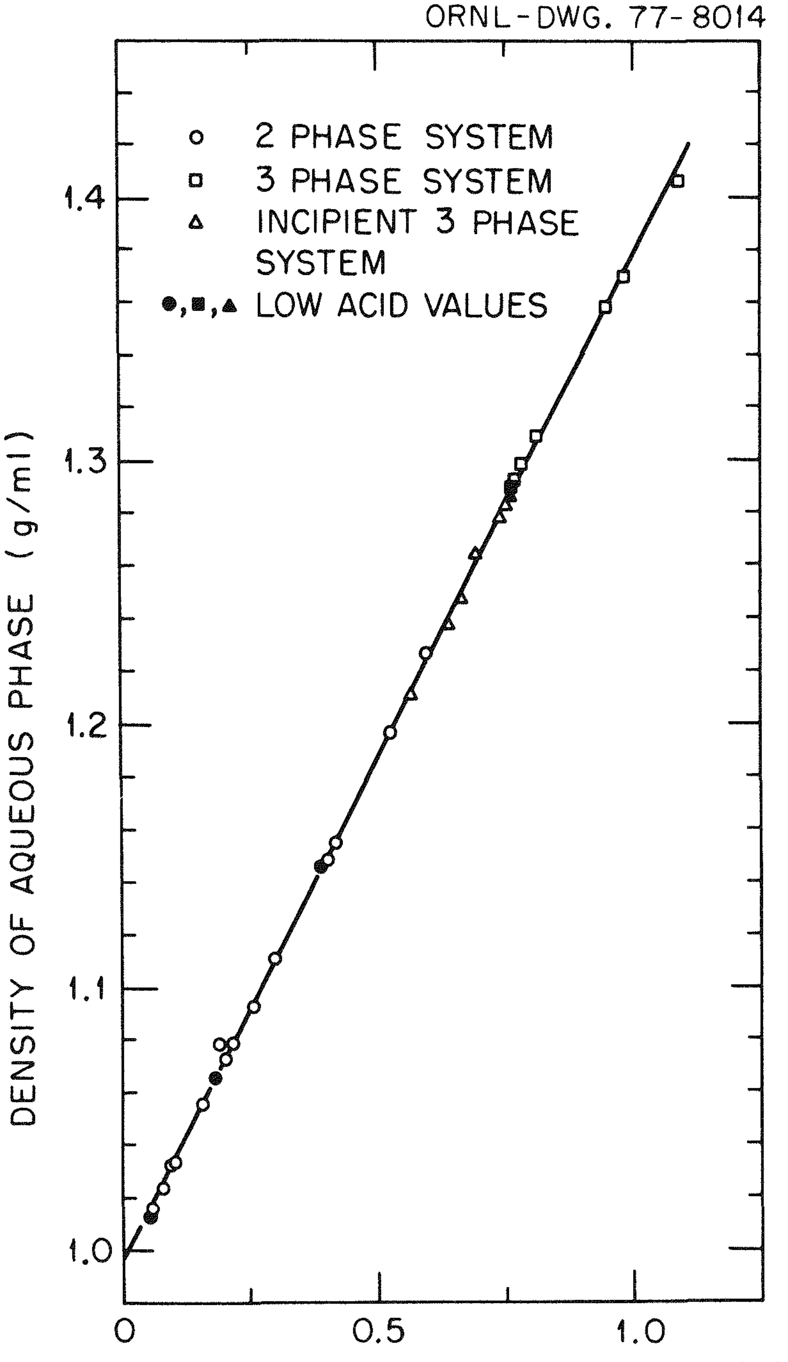

Fig. 12. Relationship of density and thorium nitrate plus free acid for the aqueous phase at 40°C.

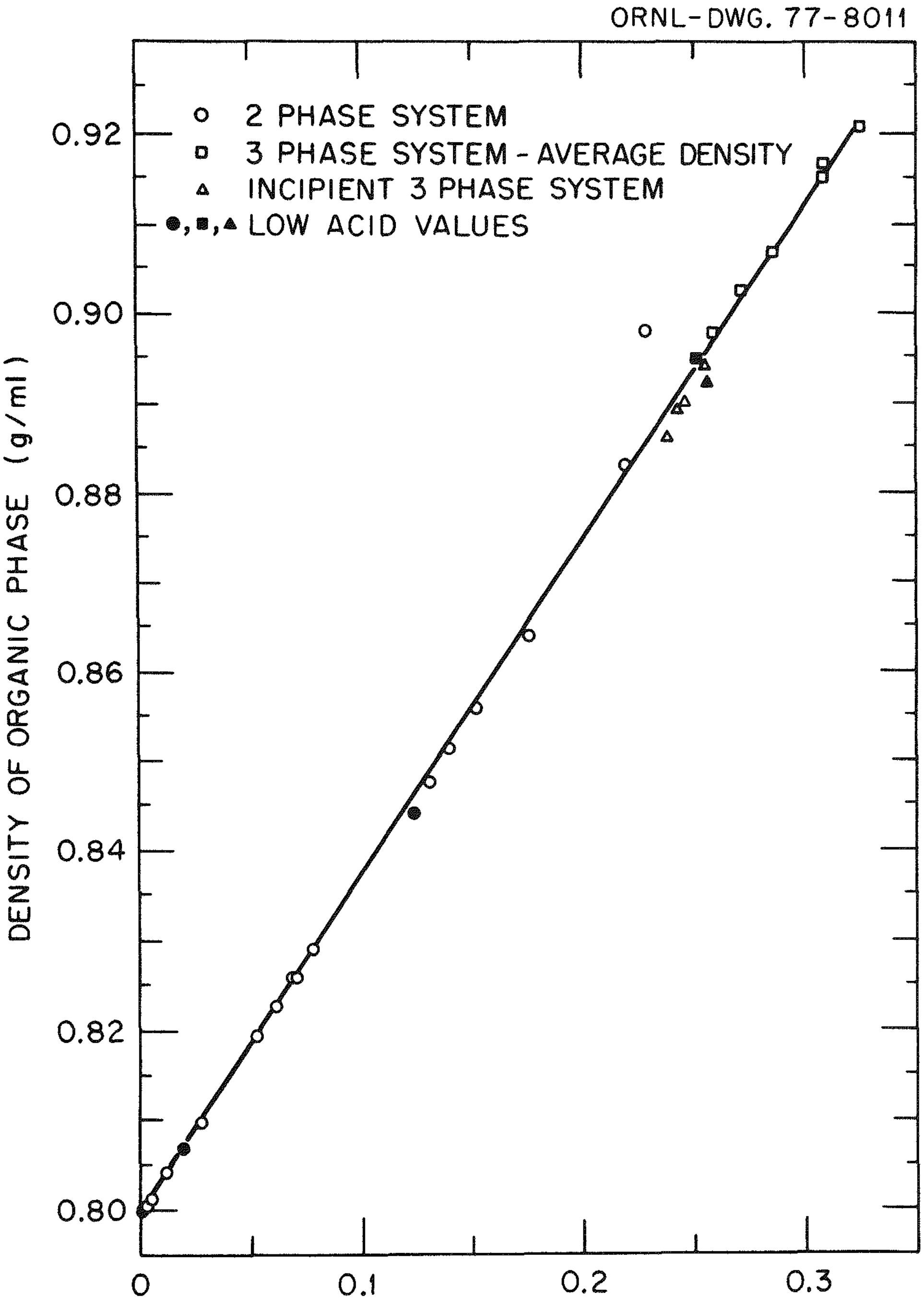

Fig. 13. Relationship of density and thorium nitrate plus free acid for the organic phase at 40°C.

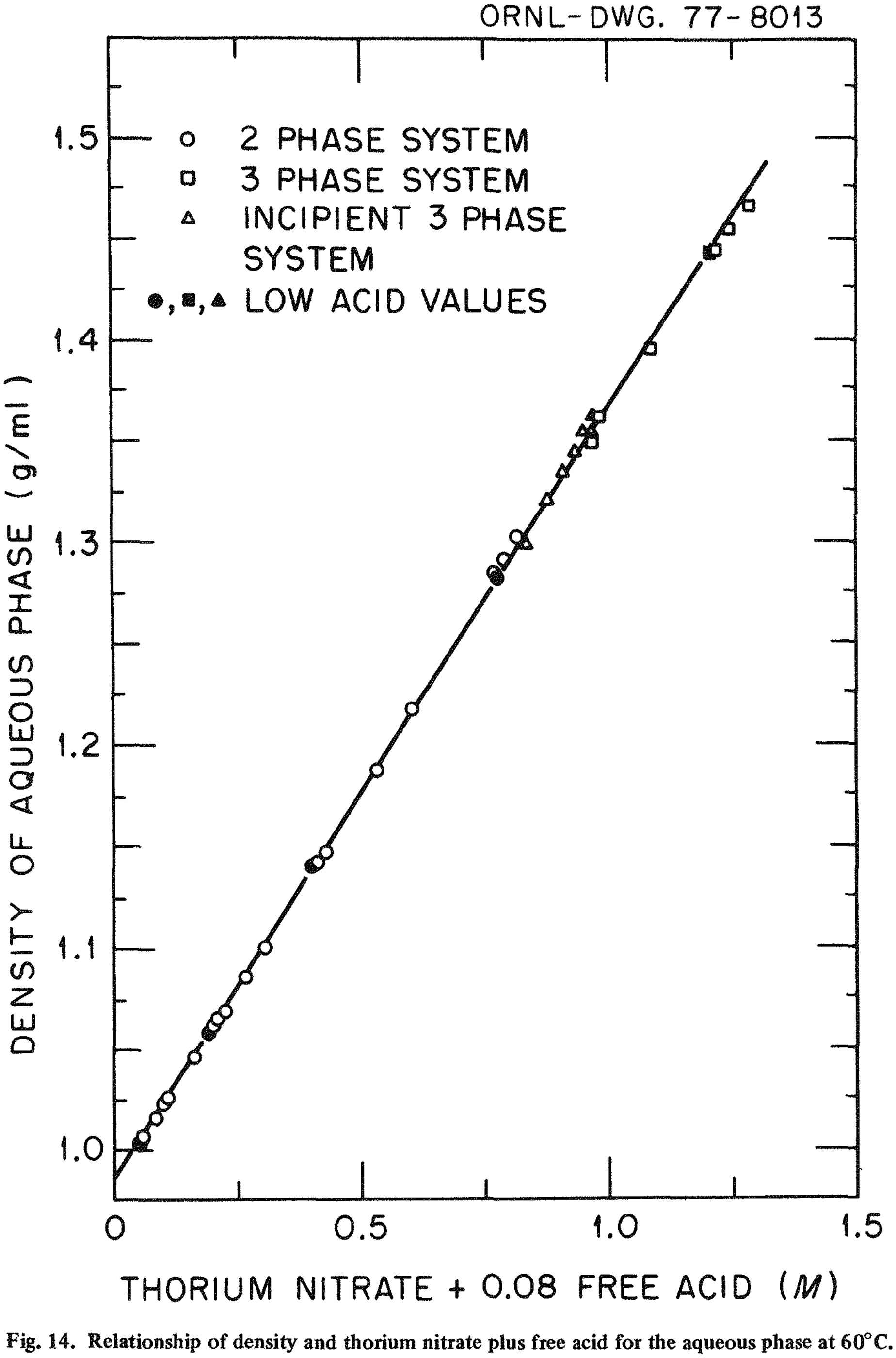

Fig. 14. Relationship of density and thorium nitrate plus free acid for the aqueous phase at 60°C.

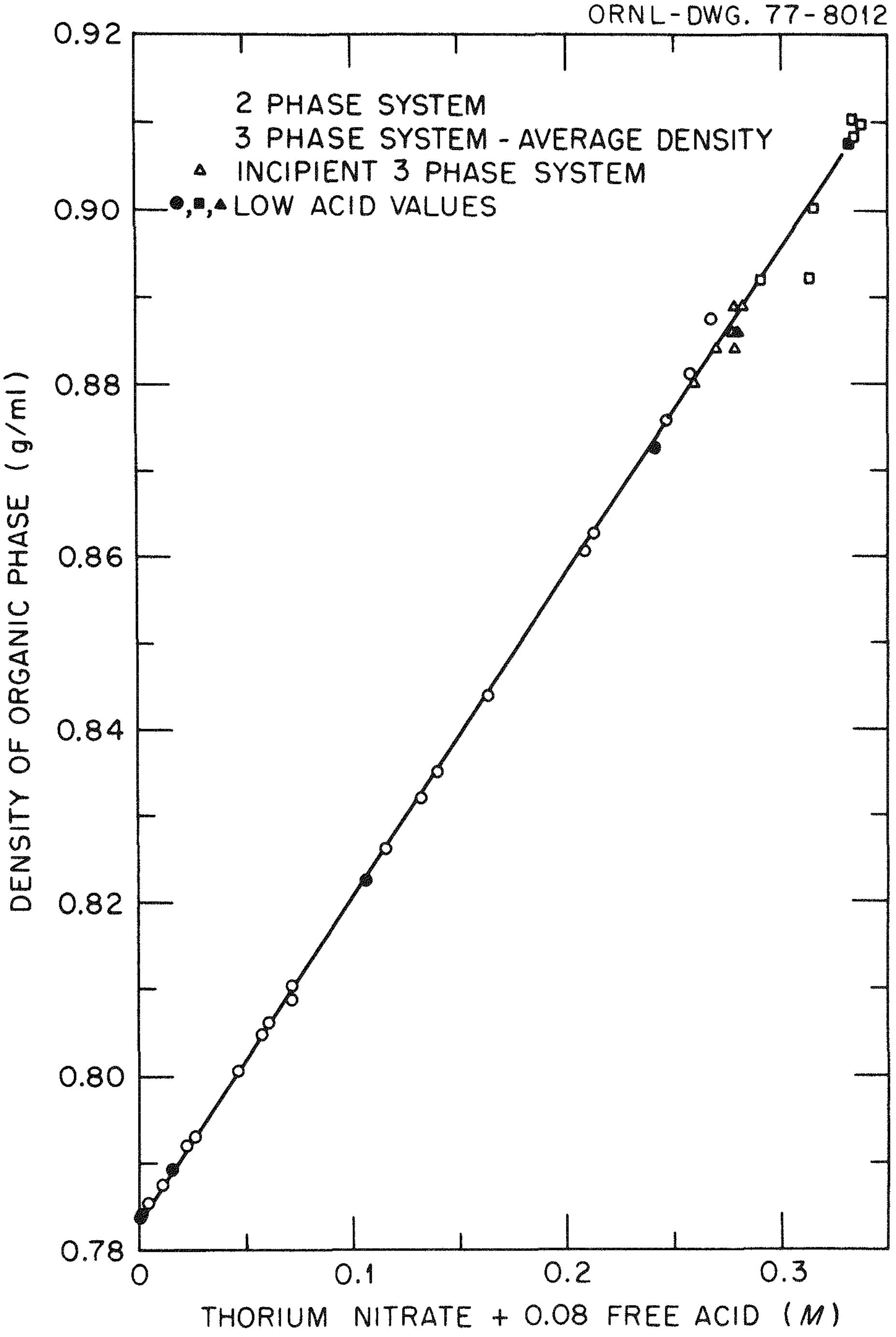

Fig. 15. Relationship of density and thorium nitrate plus free acid for the organic phase at 60°C.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of contributors. R. H. Rainey, Chemical Technology Division, provided valuable background and technical advice. J. E. Attrill, Analytical Chemistry Division, provided special analyses of the starting materials. The members of Analytical Chemistry Division's General Analytical Laboratory, under the direction R. R. Rickard, provided the analyses of samples generated by the program.

REFERENCES

1. A. T. Gresky, "Solvent Extraction Separation of ^{233}U and Thorium from Fission Products by Means of Tributyl Phosphate, " in *Proc. International Conf. Peaceful Uses of Atomic Energy* **9**, 505–10, Geneva, Switzerland (1955).
2. W. O. Haas, Jr. and D. J. Smith, *Thorex Development at KAPL,* General Electric Company, KAPL-1306 (May 1956).
3. R. H. Rainey, A. B. Meservey, and R. G. Mansfield, *Laboratory Development of the Thorex Process Progress Report,* ORNL-2591 (December 1955 to January 1958).
4. R. H. Rainey and J. G. Moore, *Nucl. Sci. Eng.* **10**, 367–71 (1961).
5. W. W. Shulz and E. E. Voiland, *Studies of the System: Thorium Nitrate, Nitric Acid, Water, Tributyl Phosphate and Amsco 125-90W,* General Electric Company, HW-32417 (December 17, 1954).
6. W. S. Groenier, *Calculations of the Transient Behaviour of a Dilute-Purex Solvent Extraction Process Having Application to the Reprocessing of LMFBR Fuels,* ORNL-4746 (April 1972).
7. R. H. Rainey and S. B. Watson, *Trans. Am. Nucl. Soc.* **22**, 315–17 (1975).
8. *Standard Method of Test for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*, D-2887-73, American Society for Testing and Materials, Philadelphia, Pa. (1973).
9. J. E. Attrill, Oak Ridge National Laboratory, Oak Ridge, Tenn., Personal communication, 1976.
10. H. Flaschka and A. J. Barnard, *Chemist-Analyst* **47**, 78 (1958).
11. S. B. Savin, *Talanta* 8, 673-85 (1961).
12. R. E. Shank, *Analytical Methods for the Remote and Service Analysis Laboratory of the Idaho Chemical Reprocessing Plant,* Allied Chemical Company, ICP-1029 (1973).
13. D. Trammer, Allied Chemical Company, Idaho Falls, Idaho, personal communication, 1976.
14. K. Alcock, *Trans. Faraday Soc.* **52**, 39–47 (1956).
15. H. A. C. McKay, G. N. Naish, and D. Scargill, *The Extraction of Thorium by Tributyl Phosphate,* Atomic Energy Research Establishment, AERE C/R 1168 (Oct. 8, 1953).
16. T. V. Healy and H. A. C. McKay, *Trans. Faraday Soc.* **52**, 633–42 (1956).

APPENDIX A

Derivation of the Free Acid Coefficient, 0.08

By assigning the definitions shown to the variables listed (in g/ml),

a = concentration of $Th(NO_3)_4$,

b = concentration of HNO_3,

c = concentration of solvent,

p_1 = density of solvent,

p_2 = density of solution,

the density of a solution can be expressed as a sum of the concentration of its constituents

$$p_2 = a + b + c \ . \tag{1}$$

If the amount of solvent excluded when $Th(NO_3)_4$ and HNO_3 are dissolved is proportional to the quantity of each, and the solvent excluded for each is independent of that excluded by the other while volume of the solution remains constant, the concentration of the solvent can be expressed as

$$c = C_1 - f_1 a - f_2 b \ , \tag{2}$$

where f_1 = exclusion factor for $Th(NO_3)_4$, and f_2 = exclusion factor for HNO_3.

By combining Eqs. (1) and (2), the following is obtained:

$$p_2 = (1 - f_1)\left[a + \frac{(1 - f_2)b}{(1 - f_1)}\right] + p_1 \ . \tag{3}$$

The combined equation is a straight line with slope of $(1 - f_1)$, and intercept = p_1 when p_2 is plotted vs $a + [(1 - f_2)/(1 - f_1)]b$.

Equation (3) can be converted into molar concentration terms and molar exclusion factors using the following identities:

C_{Th} = concentration of $Th(NO_3)_4$, M

$$= \frac{a}{0.48006} \ ;$$

C_H = concentration of HNO_3, M

$$= \frac{b}{0.063013} \ ;$$

$$f_1 = \left(\frac{1000}{480.06}\right) fM_1 = 2.083\, fM_1 \ ;$$

$$f_2 = \left(\frac{1000}{63.013}\right) fM_2 = 15.87\, fM_2 \ ;$$

where fM_1 = molar exclusion factor for $Th(NO_3)_4$, and fM_2 = molar exclusion factor for HNO_3.

By substituting the molar concentration and exclusion terms in Eqs. (1) and (2), the following expressions are obtained:

$$p_2 = 0.48006\, C_{Th} + 0.063013\, C_H + c \ , \tag{4}$$

$$c = p_1 - fM_1 C_{Tg} - fM_2 C_H \ . \tag{5}$$

Equations (4) and (5) can be combined to express the density of the solution p_2 as

$$p_2 = (0.48006 - fM_1) \left[C_{Th} + \left(\frac{0.063013 - fM_2}{0.48006 - fM_1}\right) C_H \right] + p_1 \ . \tag{6}$$

Equation (6) is a straight line with a slope of $(0.48006 - fM_1)$ and an intercept p_1 (density).

The coefficient of the free acid term, with the linear relationship

$$\frac{(0.063013 - fM_2)}{(0.48006 - fM_1)} \ ,$$

was determined by a least squares fit of the experimental data to be equal to 0.08.

ORNL/TM-7240
Dist. Category UC-86
(Applied)

INTERNAL DISTRIBUTION

1. W. J. Armento
2. W. D. Arnold
3. S. M. Babcock
4. J. T. Bell
5–9. W. D. Burch
10. L. T. Corbin
11–14. D. A. Costanzo
15. A. B. Crawford
16. D. J. Crouse
17. R. D. Ehrlich
18. W. W. Evans
19. W. S. Groenier
20. P. A. Haas
21. S. J. Hurrell
22. R. D. Hurt
23. R. T. Jubin
24. L. J. King
25. J. Q. Kirkman
26. J. B. Knauer
27. C. E. Lamb
28. R. E. Leuze
29. R. S. Lowrie
30. J. C. Mailen
31–35. J. L. Marley
36. J. L. Martin
37. J. F. Mincey
38. A. D. Mitchell
39. R. E. Norman
40. E. D. North
41–42. R. H. Powell
43. B. E. Prince
44. H. Postma
45. A. D. Ryon
46. J. H. Shaffer
47. W. D. Shults
48. B. B. Spencer
49. D. W. Swindle
50. O. K. Tallent
51. L. M. Toth
52. W. E. Unger
53. V. C. A. Vaughen
54. B. L. Vondra
55–59. A. J. Weinberger
60. M. E. Whatley
61. R. G. Wymer
62. Manson Benedict (consultant)
63–64. Laboratory Records
65. Laboratory Records, ORNL RC
66. ORNL Patent Office
67. Nuclear Safety Information Center

EXTERNAL DISTRIBUTION

68–69. W. W. Ballard, Chief, Nuclear Fuel Cycle Programs Branch, Division of Nuclear Power Development, DOE, Washington, DC 20545
70. Office of Assistant Manager, Energy Research and Development, DOE-ORO, Oak Ridge, Tennessee 37830
71–160. Given distribution as shown in TID-4500 under UC-86, Consolidated Fuel Reprocessing Category (Applied)