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STRUCTURAL EFFECTS OF β-DIKETONES ON THE ENHANCEMENT OF EXTRACTION OF URANIUM BY THE SYNERGIST TRIBUTYL PHOSPHATE

By

KENNETH BATZAR

A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy,
The City University of New York.

1966

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This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

April 20, 1966
date

Richard H. Wiley
Chairman of Examining Committee

April 20, 1966
date

Richard H. Wiley
Executive Officer

Horst Hoyer

Joseph Gluckstein

David E. Goldberg
Supervisory Committee

The City University of New York

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SYMBOLS

The following symbols are used throughout this paper. Other symbols, used less frequently, will be explained as they are introduced.

[ ] - concentration of species in aqueous phase indicated in moles per liter.

( ) - concentration of species in organic phase indicated in moles per liter.

HT - β-diketone.

T^- - enolate ion of β-diketone.

S - synergist.

D_o - distribution coefficient in absence of synergist.

D - distribution coefficient in presence of synergist.

K_t - equilibrium constant for the extraction reaction in the absence of synergist.

K_{ts} - equilibrium constant for the extraction reaction in the presence of synergist.

K_s - equilibrium constant for the interaction of synergist with chelate.

AA - 2,4-pentanedione (acetylacetone).

BA - 1-phenyl-1,3-butanedione (benzoylacetone).

BTA - 4,4,4-trifluoro-1-phenyl-1,3-butanedione (benzoyltrifluoroacetone).

DBM - 1,3-diphenyl-1,3-propanedione (dibenzoylmethane).

FTA - 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione (furoyltrifluoroacetone).

MeTTA - 4,4,4-trifluoro-2-methyl-1-(2-thienyl)-1,3-butanedione.

TA - 1-(2-thienyl)-1,3-butanedione (thenoylacetone).

TTA - 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone).

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TBP - tributyl phosphate.

d_b - number of micrograms of metal per ml in benzene phase.

d_a - number of micrograms of metal per ml in aqueous phase.

V - total volume of variant added.

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INTRODUCTION

HISTORICAL.

The word "synergism" was first coined by Baes and coworkers[1] to describe their discovery of a definite enhancement of the extraction of uranium from aqueous solution by a mixture of an acidic dialkyl phosphate and certain neutral organophosphorus esters, the resulting mixture giving a better extraction of uranium than either the acid or neutral phosphate alone. These workers considered that this synergic (synergistic) enhancement was limited to dialkyl phosphoric acid-neutral reagent combinations and that, out of several elements studied, uranium, as uranyl ion, was the only one which was extracted synergically.

A few years prior to the work of Baes, Cunningham[2] showed that mixtures of thenoyltrifluoroacetone (TTA) and tributyl phosphate (TBP) in benzene would extract praseodymium and neodymium from nitrate solutions to a greater extent than either reagent alone. He attributed this increase to the probable formation of the complexes $M(TTA)_3$, $M(TTA)_2(TBP)NO_3$,$M(TTA)(TBP)_2(NO_3)_2$ and $M(TBP)_3(NO_3)_3$. Irving and Edgington[3] repeated the work of Baes substituting TTA for the acidic dialkyl phosphate and obtained a much larger enhancement for the extraction of uranium. They predicted that the synergic effect should not be observed in the extraction of the quadrivalent actinides because the quadrivalent actinides are coordinately saturated by TTA. However, in a later study[4] on the extraction of the quadrivalent actinides with TTA and tributyl phosphate from nitric acid solution they in fact observed a synergic effect. Their

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conclusions were identical to those of Cunningham concerning the species present.

Healy[5] extended the work of Irving and Edgington by substituting a hydrochloric acid solution for nitrate solution and showed similar very large enhancements for bivalent, tervalent and quadrivalent metals. He explained his results in terms of an addition without replacement and concluded that the difference in the aqueous phase from that used in previous work permitted the occurrence of an addition reaction as opposed to a replacement reaction. In a nitrate-containing medium there is a competition between the extraction by tributyl phosphate of the uranyl nitrate complex and the extraction by the β-diketone of the uranyl ion. The consequence is a mixed ligand complex which contains uranium, nitrate, tributyl phosphate and the β-diketone. In a chloride medium, where there is no competition due to the extraction of a uranyl chloride complex by tributyl phosphate, the synergism occurs by means of an addition reaction. Healy suggested that an aquo-metal-β-diketone complex such as $UO_2(TTA)_2(H_2O)_x$ is rendered less hydrophilic by the substitution of a neutral ester for the water group or groups producing a species such as $UO_2(TTA)_2(TBP)_x$.

Healy[6] showed that 3-nonanol and N,n-butyl acetanilide exert synergic behavior on the thorium-and uranyl-TTA systems. Newman and Klotz[7] showed that trioctylamine also exerts synergic behavior on the thorium system. After studying the interactions between trioctylamine and hydrochloric acid, and trioctylamine and TTA[8,9] they concluded that trioctylamine hydrochloride adds to the thorium-β-diketone complex.

Spectrophotometric studies of the uranyl-β-diketone-tributyl phosphate system performed by Healy[10,11] led him to the conclusion that there is a complex formed by TTA and tributyl phosphate whether the

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β-diketone is coordinated to the uranyl ion or not. The conditions for this interaction depend upon the concentration of tributyl phosphate and water in the system. Healy did not postulate the interaction site on the β-diketone coordinated to uranyl ion. He did state that in the absence of metal ion the interaction involved hydrogen bonding between tributyl phosphate and the enol form of the β-diketone. Interaction with the ketohydrate form of the β-diketone was ruled out because complexation increased as the concentration of water decreased in the system and because a ketohydrate spectrum was not found.

Newman[12] evaluated K_s for systems M/TTA/S where $K_s = \frac{(MT_nS_p)}{(MT_n)(S)^p}$ S was either tributyl phosphate or trioctyl phosphine oxide; M was thorium, uranyl, americium, curium, prometheum, thulium or calcium; and the diluent was benzene or cyclohexane. K_s remained constant in systems where diluent, synergist and value of p were the same and only the metal ion was changed. Newman argued that since the synergic constant is a function only of the number of addenda per molecule and not a function of the metal involved, then the synergist most likely forms a bond with one of the β-diketone molecules attached to the metal, and not with the metal itself. If bonds existed between the synergic agent and the metals there presumably should be differences in the values of K_s which reflect the differences in the metals.

E. Szábo[13] studied the extraction of uranyl ion with acetylacetone (AA) and TBP. This was the first report of a synergic enhancement of the extraction of a metal ion with a β-diketone other than TTA. Although he was able to show an enhancement of extraction, he did not postulate what species were formed and the mechanism by which the extraction took place.

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STATEMENT OF THE PROBLEM.

The purpose of this thesis is to determine the conditions necessary for obtaining and improving synergic enhancement of the solvent extraction of uranium, the nature of the composition of the synergic complex found, and how the synergic agent is bonded in this complex. Previous investigators have limited their work primarily to the use of TTA as the extractant of uranium when studying synergic effects. These investigators, while offering a great deal of data concerning the uranyl-TTA-TBP system, provide contradictory statements as to the bonding in the synergic complex and do not state the conditions necessary for synergism to occur.

Thus, data were accumulated for various extractions where the structure of the β-diketone was changed (Table I, p.5) so that possible sites for addition of the synergist in the complex were changed. Synergism occurred in all the systems studied, which provided insight as to how the synergist bonded in the complex. The stoichiometry of the complexes was also determined and conditions were established which would provide a greater degree of synergic extraction for uranium.

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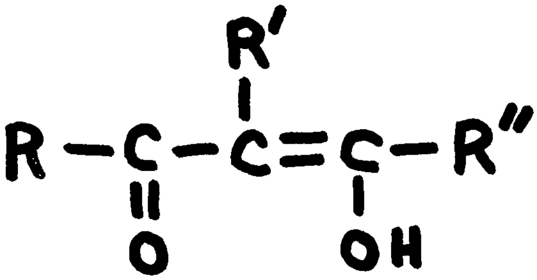
TABLE I

β-DIKETONE STRUCTURES



$$R-\underset{\underset{O}{\|}}{C}-\overset{\overset{R'}{|}}{C}=\underset{\underset{OH}{|}}{C}-R''$$

β-Diketone	Abbrev.	R	R′	R″
Benzoyltrifluoroacetone	BTA	phenyl	H	CF_3
Thenoyltrifluoroacetone	TTA	2-thienyl	H	CF_3
Furoyltrifluoroacetone	FTA	2-furyl	H	CF_3
Acetylacetone	AA	CH_3	H	CH_3
Benzoylacetone	BA	phenyl	H	CH_3
Dibenzoylmethane	DBM	phenyl	H	phenyl
Thenoylacetone	TA	2-thienyl	H	CH_3
4,4,4-Trifluoro-2-methyl-1-(2-thienyl)1,3-butanedione	MeTTA	2-thienyl	CH_3	CF_3

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CALCULATION METHODS

DISTRIBUTION COEFFICIENT.

Solvent extraction is based on the distribution of a solute between two immiscible phases. For this case the classical phase rule of Gibbs can be applied

$$P + F = C + 2 \qquad (1)$$

where P is the number of phases, F the number of degrees of freedom, and C the number of components. According to equation (1) a system consisting of two immiscible solvents and one solute distributed between them has one degree of freedom at constant temperature and pressure. Thus if the concentration of the solute in one phase is constant, the concentration of the solute in the other phase is also fixed. The relationship between the concentration of solute in each of the solvent phases led to Nernst's formulation of the distribution law[14] on the basis of experiments by Berthelot and Jungfleisch.[15]

The concentration ratio of the solute in the two phases at equilibrium is called the partition coefficient, p, and it can be expressed by the following equation:

$$p = C_{org}/C$$

where C_{org} and C denote the concentration of the distributed compound in the organic and aqueous phases respectively assuming activity coefficients are constant.

When an ion with a charge n+ is equilibrated between an organic and an aqueous phase (containing solvent molecules B and H_2O), then in the

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presence of an organic reagent, HA, complexes of the general composition $M_mA_n(OH)_p(HA)_rB_s(H_2O)_t$ may be formed. Rydberg[16,17] considered the formation of such a hypothetical complex and showed that its composition and stability could be determined from measurements of the distribution coefficient, D, of the total metal between the organic and aqueous phases as a function of the different variables. The following equation will be valid for the distribution ratio of the metal M between the organic and aqueous phases:

$$D = \frac{\text{Total concentration of metal species in the organic phase}}{\text{Total concentration of metal species in the aqueous phase}} \qquad (2)$$

If the aliquots withdrawn from both phases are equal this definition may be replaced by

$$D = \frac{\text{Micrograms of metal in organic aliquot}}{\text{Micrograms of metal in aqueous aliquot}} \qquad (3)$$

since the same value for atomic weight of the metal would be used to determine the concentration of all species in both phases.

The species formed when a ligand is added to an organic-aqueous phase system containing a metal ion may be distributed between the two phases depending on the charge of the species and their affinities for either phase. In a system containing a tetracoordinate metal ion, M^{++}, a β-diketone, HT, and a non-complexing aqueous medium the least complicated reaction that can be written for the coordination of the metal ion is as follows:

$$M^{++} + 2\,HT \rightleftharpoons MT_2 + 2\,H^+$$

Charged species are present mainly in the aqueous phase and neutral species in the organic phase. The equilibrium constant for this reaction, K_t, is

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represented as follows:

$$K_t = \frac{(MT_2) \quad [H^+]^2}{[M^{++}] \quad (HT)^2} \qquad (4)$$

One may express the distribution coefficient for this system as follows:

$$D_o = \frac{(MT_2)}{[M^{++}]} \quad = \quad K_t \ (HT)^2 \ [H^+]^{-2} \qquad (5)$$

since activity coefficients are assumed to be constant.

$$\log D_o = \log K_t + 2 \log (HT) - 2 \log [H^+] \qquad (6)$$

A plot of log D_o vs. pH at constant HT concentration or log D_o vs. log (HT) at constant pH should give information as to whether the reaction is correct as written. The slope of this plot should have the same numerical value as the number of ligands that have added to each metal ion. Any deviations from a slope of two are indicative of reactions other than that represented above.

If synergist, S, is added to the above system the most straightforward reaction that can occur is

$$M^{++} + 2\ HT + x\ S \rightleftharpoons MT_2S_x + 2\ H^+ \qquad (7)$$

The equilibrium constant for this reaction, K_{ts}, is represented as follows:

$$K_{ts} = \frac{(MT_2S_x) \quad [H^+]^2}{[M^{++}] \ (HT)^2 (S)^x} \qquad (8)$$

$$D = \frac{(MT_2S_x)}{[M^{++}]} \quad = \quad K_{ts} \ (HT)^2 (S)^x \ [H^+]^{-2} \qquad (9)$$

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$$\log D = \log K_{ts} (S)^x + 2 \log (HT) - 2 \log [H^+] \qquad (10)$$

The slope of the plot of log D vs. pH at constant HT concentration or log D vs. log (HT) at constant pH should have the same numerical value as the number of β-diketone molecules that coordinate to the metal ion in the presence of synergist. Once again deviations from slope two are indicative of reactions other than the equilibrium represented by equation (7).

The simplest organic phase reaction which will produce the species MT_2S_x is as follows:

$$MT_2 + x\ S \rightleftharpoons MT_2S_x \qquad (11)$$

The equilibrium constant for this reaction, K_s, is represented as

$$K_s = \frac{(MT_2S_x)}{(MT_2)(S)^x} \qquad (12)$$

The experimental distribution coefficient, D_s, obtained by varying concentration of synergist while keeping all other concentration terms constant may be written as

$$D_s = D_o + D = \frac{(MT_2) + (MT_2S_x)}{[M^{++}]} = \frac{(MT_2) + K_s\ (MT_2)(S)^x}{[M^{++}]} \qquad (13)$$

Combining equations (4), (5), (8) and (13) yields

$$D_s - D_o = K_{ts} (HT)^2 (S)^x [H^+]^{-2} \qquad (14)$$

$$\log (D_s - D_o) = \log K_{ts} (HT)^2 [H^+]^{-2} + x \log S \qquad (15)$$

The slope of the plot of log $(D_s - D_o)$ vs. log (S) will yield the value of x, the number of synergic addenda per molecule of chelate since the first term of the right side of equation (15) is constant.

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EQUILIBRIUM CONSTANTS.

Equilibrium constants can be evaluated for the reactions written above with the aid of the same plots that are used to determine the number of molecules bonded to metal ion. From equation (6) the plot of log D_o vs. log (HT) has an intercept equal to log K_t - 2 log $[H^+]$. If the pH is known, log K_t can be evaluated.

If the number of synergic addenda is equal to one, then equation (10) may be altered to read

$$\log D \;=\; \log K_{ts}\,(S)\,[H^+]^{-2} \;+\; 2\log\,(HT)$$

If the pH and concentration of synergist are known log K_{ts} can be evaluated from the intercept of the plot of log D vs. log (HT). This equation was used in the studies presented.

If log K_{ts} and log K_t are known for a β-diketone then log K_s may be obtained by subtracting log K_t from log K_{ts} because $K_{ts}/K_t = K_s$.

METHOD OF LEAST SQUARES.

The data were subjected to the method of least squares to determine the slopes and intercepts of the various plots. This work was performed on an I.B.M. 1620 Model I computer using a modified subroutine of K. Wiberg.[18]

Although least squares analysis is an accepted method for determining the slope and intercept of the best straight line through experimental points it does not necessarily apply to the data appearing in this work. The free ligands present at equilibrium lend themselves to side reactions which may cause deviations in the slopes of the experimental plots. A

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more reliable method is to analyze the experimental data directly. Any deviations from linearity or integral slope at either end of the plot lead to conclusions about side reactions.

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EXPERIMENTAL

EXTRACTION PROCEDURE.

For these studies it was necessary to use a titration apparatus which provided for stirring, temperature control, electrodes for pH determination and an opening for removing aliquots of the aqueous and organic phases. The vessel designed for the titrations was made by sealing three extra necks onto a standard 200-ml. round-bottomed flask which had been encased in a water jacket. A cork in the center neck held the buret. The other necks provided access to a dip tube, a glass electrode and a silver - silver chloride electrode.

An Instrumentation Laboratory Model 135A electrometer was used as a potentiometer, together with a glass electrode (Beckman no. 40498) and a fiber junction silver - silver chloride electrode with a salt bridge containing a solution saturated with respect to silver chloride, 0.01 M with respect to lithium chloride and 1.99 M with respect to lithium perchlorate.

The solution in the flask was stirred with a magnetic stirrer and kept at 30.0° by pumping water from a constant temperature bath through the water jacket.

Five general types of extraction experiments were performed, the procedures for which are outlined below.

VARIANT - TRIBUTYL PHOSPHATE - Sixty ml of a solution containing perchloric acid and 2.0 M with respect to lithium perchlorate (pH = 3.5 for AA, BA, TA and DBM; pH = 1.2 for BTA, FTA, and TTA) was stirred with sixty ml of a 0.2 M solution of β-diketone in benzene for one hour at 30.0°. Fifty ml of this equilibrated aqueous phase was

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then pipetted into the four-necked flask to which had been added 1.00 ml of a uranyl perchlorate solution containing five mg of uranium in 2.0 M lithium perchlorate (final concentration of uranium - 4×10^{-4} M). Fifty ml of a 0.2 M solution of β-diketone in benzene was added to this aqueous phase and vigorously stirred for forty minutes at which time 1.00 ml aliquots were removed from each phase. The concentration of TBP was changed by discharging quantities of 0.987 M TBP in benzene from a micro buret. After each aliquot of TBP was added the contents of the flask was stirred for ten minutes and a 1.00 ml sample removed from each phase. The sample was taken from the aqueous phase by blowing air through a dip tube several times, which displaced the benzene phase permitting the aqueous phase to enter. A 1 ml pipet was inserted into the tube to remove the sample. This procedure was followed for each change in TBP concentration until a concentration of 0.2 M TBP was obtained and at least twelve aliquots had been added. The temperature was kept at $30.0 \pm 0.1^{\circ}$ throughout the experiment. The pH was kept constant by the addition of small quantities of base or acid to the aqueous phase. To prevent hydrolysis, additions were made carefully to avoid local excess of acid or base. A solution 0.1 M with respect to lithium hydroxide and 1.9 M with respect to lithium perchlorate was added if the contents of the flask became too acidic, or a solution 0.1 M with respect to perchloric acid and 1.9 M with respect to lithium perchlorate if the contents became too basic.

After the experiment was complete, the glass and silver - silver chloride electrodes were placed in an aqueous solution 0.0099 M with respect to perchloric acid and 1.99 M with respect to lithium perchlorate and kept at 30.0°. The e.m.f. obtained from this solution was used to

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determine $E^{o'}$ for the electrode pair and the pH was obtained by substitution into the Bates equation[19] which follows:

$$E_1 = E^{o'} + \frac{RT}{F} \ln \frac{1}{[H^+]} \qquad (16)$$

E_1 is the e.m.f. value in millivolts of the aqueous solution in the four-necked flask and $E^{o'}$ is obtained by adding 120.3 millivolts to the e.m.f. reading of the solution 0.0099 M with respect to perchloric acid and 1.99 M with respect to lithium perchlorate. The constant $\frac{2.30\ RT}{F}$ is equal to 60.1 because all studies were performed at 30.0°C.

VARIANT - pH - NO SYNERGIST PRESENT - Sixty ml of a 2.0 M lithium perchlorate solution (pH = 3.0) was stirred with sixty ml of a 0.2 M solution of β-diketone in benzene for one hour at 30.0°. Fifty ml of this equilibrated aqueous phase was then pipetted into the four-necked flask to which had been added 1.00 ml of a solution 0.02 M with respect to uranyl perchlorate and 2.0 M with respect to lithium perchlorate. Fifty ml of a 0.2 M solution of β-diketone in benzene was added to this aqueous phase and stirred for forty minutes at which time 1.00 ml aliquots were removed from each phase. The pH was varied from 3.0 to 1.0 by the addition of 1.994 M perchloric acid in sufficient quantities to insure that the pH change was at least 0.1 unit between additions. The contents of the flask was stirred for ten minutes to assure equilibration of the phases and a 1.00 ml sample removed from each phase. The e.m.f. of the system was measured after the samples were removed. The pH of the samples was obtained by use of the e.m.f. readings as described above and all the runs were performed at 30.0 ± 0.1°.

VARIANT - pH - SYNERGIST PRESENT - The procedure used was the same as for "no synergist present" with the following exceptions:

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Sixty ml of a 2.0 M lithium perchlorate solution was stirred for one hour with sixty ml of a benzene solution 0.2 M with respect to β-diketone and 0.2 M with respect to TBP. Fifty ml of a benzene solution 0.2 M with respect to β-diketone and 0.2 M with respect to TBP was added to fifty ml of the equilibrated aqueous phase to which the uranium had been added. The pH was varied from approximately 2.5 to 0.5, since higher acidities were necessary to obtain meaningful distribution coefficients in the presence of TBP.

VARIANT - β-DIKETONE - NO SYNERGIST PRESENT - Fifty ml of benzene, 50.0 ml of a 2.0 M lithium perchlorate solution, and 1.00 ml of a solution 0.02 M with respect to uranyl perchlorate, and 2.0 M with respect to lithium perchlorate were added to the four-necked flask. Additions of 2.00 M β-diketone in benzene were made so that initially the concentration of β-diketone in the flask was 0.001 M and finally 0.200 M. At least ten concentrations were obtained between the extremes. After allowing 10 minutes stirring time for attainment of equilibrium, 1.00 ml aliquots were removed from each phase at each concentration. The pH was kept constant throughout the experiment as explained previously. After the concentration of β-diketone had been raised to 0.2 M, two separate portions of known amounts of benzene were added to lower the β-diketone concentration, and samples were withdrawn after stirring. This procedure was performed to ascertain whether the system was at equilibrium, since the same distribution coefficient should be obtained, within experimental error (±10%), for the same concentration of β-diketone no matter how this concentration is obtained.

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VARIANT - β-DIKETONE - SYNERGIST PRESENT - The procedure was the same as directly above except the aqueous phase was shaken for one hour with 0.20 M TBP, prior to use, and the four-necked flask contained fifty ml of 0.20 M TBP in benzene instead of benzene itself. After the concentration of β-diketone had been raised to 0.2 M, two separate portions of known amounts of 0.2 M TBP were added to lower the β-diketone concentration.

KINETICS PROCEDURE.

Eighty ml of a solution 2.0 M with respect to lithium perchlorate and pH = 3.0 was stirred with eighty ml of a 0.2 M solution of β-diketone in benzene or eighty ml of a benzene solution 0.2 M with respect to β-diketone and 0.2 M with respect to tributyl phosphate, whichever was appropriate. Seventy five ml of this equilibrated aqueous phase was then pipetted into a four-necked flask to which 1.0 ml of a uranyl perchlorate solution containing five mg of uranium in 2.0 M lithium perchlorate had been added. Seventy five ml of the appropriate organic phase was added to this aqueous phase and vigorously stirred for forty minute intervals at which time 1.00 ml aliquots were removed from each phase and the e.m.f. of the system was obtained. After four such intervals two 25 ml aliquots of each phase were removed, and an aqueous and an organic aliquot were added to each of two four-necked flasks. The pH was adjusted to 2.0 in one flask and to 1.0 in the second. The solutions in each flask were stirred for allotted time intervals after which 1.00 ml aliquots were removed from each phase, and the e.m.f. of the system recorded.

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PREPARATION AND STANDARDIZATION OF REAGENTS.

β-Diketones. All the β-diketones except 4,4,4-trifluoro-2-methyl-1-(2-thienyl)-1,3-butanedione and 2,4-pentanedione were purchased as reagent grade chemicals and were not further purified.

4,4,4-Trifluoro-1-(2-Thienyl)-1,3-Butanedione. The compound was obtained from Penisular ChemResearch, Inc., P.O. Box 3597, Gainesville, Florida. M.p. 41-42°; reported[20] 42.5-43.2°.

4,4,4-Trifluoro-1-Phenyl-1,3-Butanedione. The compound was obtained from Penisular ChemResearch Inc., P.O. Box 3597, Gainesville, Florida. M.p. 38-40°; reported[20] 39-40.5°.

4,4,4-Trifluoro-1-(2-Furyl)-1,3-Butanedione. The compound was purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York. M.p. 19-21°; reported[20] 19-21°.

1-(2-Thienyl)-1,3-Butanedione. The compound was purchased from Chemical Procurement Laboratories, 18-17 130 Street, College Point 56, N.Y. B.p. 128-130°/8mm; reported[21] 129-131°/8mm.

1-Phenyl-1,3-Butanedione. The compound was purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, N.Y. M.p. 58-9°; reported[22] 59°.

1,3-Diphenyl-1,3-Propanedione. The compound was purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, N.Y. M.p. 77-8°; reported[23] 78°.

2,4-Pentanedione. The compound was obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, N.Y. It was distilled at atmospheric pressure; b.p. 138°; reported[24] 139°. A colorless product was obtained.

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4,4,4-Trifluoro-2-Methyl-1-(2-Thienyl)-1,3-Butanedione. The compound was prepared by the method of Barkley and Levine.[25] To a stirred suspension of 0.6 mole of sodium methoxide in 200 ml absolute ether was slowly added 0.3 mole of ethyl trifluoroacetate in 50 ml anhydrous ether. Then, 0.3 mole of 2-propionyl thiophene in 50 ml of anhydrous ether was added over a forty minute period and the mixture stirred at room temperature for twenty hours. The mixture was then poured onto 500 g of crushed ice and kept cold during the entire working up procedure. The basic aqueous phase was extracted with ether and then cautiously acidified with a mixture of ice and concentrated hydrochloric acid. The β-diketone precipitated as an oil and was extracted with ether. The ether was distilled after drying and the residue fractionated to give 65% yield of yellow oil. B.p. 85-7°/0.9 mm. Copper derivative melted at 202-4° as reported.[25]

$C_9H_7F_3OS$	%C	%H	%S
Calcd.	45.77	2.99	13.57
Found	45.93	3.04	13.69

TRIBUTYL PHOSPHATE - The compound was obtained from Fisher Scientific Company, Fair Lawn, New Jersey. It was purified by the method of Scruggs.[26] The product was distilled under reduced pressure; b.p. 138-9/3 mm, $n_d^{20} = 1.4244$. The reported[26] boiling point is 143-4/4 mm.

BENZENE.- The compound (A.C.S. thiophene free) was obtained from Fisher Scientific Company, Fair Lawn, New Jersey.

LITHIUM PERCHLORATE - The compound was obtained from the G. Frederick Smith Co., 867 McKinley Avenue, Columbus 22, Ohio, and was used without further purification.

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PERCHLORIC ACID - The compound was obtained from the J.T. Baker Chemical Co., Phillipsburg, New Jersey. Standard analytical procedure was used to standardize the acid.

URANYL PERCHLORATE - The compound was prepared by treating uranium trioxide, obtained from Brookhaven National Laboratory, with perchloric acid in a mole ratio of 1:2. The salt was then dissolved in sufficient 2.0 M lithium perchlorate to make a solution that contained 5 mg of uranium/ml.

THORIUM PERCHLORATE - The compound was prepared by treating thorium nitrate solution with an excess of sodium carbonate solution. The precipitate was air dried and a small amount tested for nitrate by the brown ring test. The carbonate was then treated with perchloric acid in a mole ratio of 1:4 and the perchlorate dissolved in sufficient 2.0 M lithium perchlorate to produce a solution containing 25 mg of thorium/ml.

ANALYSIS OF METAL IONS.

URANIUM - Fluorimetric determinations of uranium were carried out by the Hot Laboratory at Brookhaven National Laboratory using a slightly modified method of Centanni.[27] The accuracy of this method is ±10%.

THORIUM - Spectrophotometric determinations of thorium were performed on a Beckman DU spectrophotometer by the Hot Laboratory at Brookhaven National Laboratory using the procedure of Thomason[28] with modifications by Newman.[7] The accuracy of this method is ±2%.

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TABLE II

EXPERIMENTAL CONCENTRATIONS

β-Diketones W - AA, BA, DBM, TA ST - BTA, FTA, TTA	Variant	pH	(HT)	(S)	[U]
W	S	3.5	0.2 M	0.001 M - 0.2 M	0.0004 M
ST	S	1.2	0.2 M	0.001 M - 0.2 M	0.0004 M
W	pH - No S	3.0-1.0	0.2 M		0.0004 M
ST	pH - No S	3.0-1.0	0.2 M		0.0004 M
W	pH - S present	3.0-1.0	0.2 M	0.2 M	0.0004 M
ST	pH - S present	1.5-0.5	0.2 M	0.2 M	0.0004 M
W	HT - No S	3.0	0.01 M - 0.2 M		0.0004 M
ST	HT - No S	3.0	0.01 M - 0.2 M		0.0004 M
W	HT - S present	3.0	0.01 M - 0.2 M	0.2 M	0.0004 M
ST	HT - S present	1.5	0.01 M - 0.2 M	0.2 M	0.0004 M

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RESULTS

Values of the slopes of plots of log D vs. variant obtained by graphical methods are assembled in Tables III and IV. Table V shows the results of Least Squares analyses of these plots.

The calculated values of the logarithms of equilibrium constants are presented in Table VI. Values of K_t and K_{ts} were obtained by evaluating the intercepts of plots of log D_o vs. log (HT) and log D vs. log (HT) respectively (Figures VIII - XXIV) because variation of HT concentration was the only procedure which produced data for all the β-diketones studied. Equations (6) and (10) are the basis for such calculations. Values of K_s were obtained directly from K_t and K_{ts} since $K_s = K_{ts}/K_t$. Values of the negative logarithms of the dissociation constants[29], pK_D, which were obtained in a dioxane-water system, are also presented.

Table VII lists the values of log K_{ts} obtained from the three types of extraction studies carried out in this work. Equations (10) and (15) are the basis for these calculations. Table VIII lists the values of log K_t obtained from procedures where either pH or β-diketone was the variant. Some values of K_{ts} and K_t, variant pH, are not entered in the tables because of kinetic complications which will be explained in the Discussion Section.

In order to be able to compare the various β-diketones easily, the differences between logarithms of equilibrium constant values from Table V for each β-diketone and those for acetylacetone were tabulated. Acetylacetone was chosen as a reference and assigned a value of 1.0 in each case so that comparison may be easily made. Table IX lists the

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logarithms of the values assigned to the β-diketones.

All calculation methods are described in the preceeding section. The graphs, data for solvent extraction studies, and data for kinetic studies are collected in the appendix.

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TABLE III

SLOPES OF PLOTS LOG D VS. HT CONCENTRATION

β-Diketone	Medium	No S	Figure	S	Figure
BTA	ClO_4^-	2.0	XIII	2.0	XV
	NO_3^-	2.0	XIV		
FTA	ClO_4^-	2.0	XVIII	2.0	XIX
TTA	ClO_4^-	2.0	XXIII	2.0	XXIV
AA	ClO_4^-	2.0	VIII	2.0	IX
	$SO_4^=$			2.0	X
BA	ClO_4^-	2.0	VI	2.0	VII
DBM	ClO_4^-	2.0	XVI	2.0	XVII
TA	ClO_4^-	2.0	XXI	2.0	XXII
MeTTA	ClO_4^-			2.0	XX

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TABLE IV

SLOPES OF PLOTS LOG D VS. VARIANT

β-Diketone	Variant - pH Medium	No S	Figure	S	Figure	Variant - (S) ClO_4^- Medium	Fig.
BTA	ClO_4^-	2.0→1.0	XXVI, XXXVII	2.0	XXXIX	1.0	IV
	NO_3^-	2.0	XXXVIII				
FTA	ClO_4^-	1.4	XLII	2.0	XLIII	1.0	IV
TTA	ClO_4^-	2.0	XLVII	2.0	XLIX	1.0	V
	Cl^-	2.0	XLVIII	2.0	L		
	SO_4^-			1.3 → 0	LI		
AA	ClO_4^-	2.0	XXV	1.4	XXVI	1.0	I
	$SO_4^=$			2.0	XXVII	1.0 ($SO_4^=$)	II
BA	ClO_4^-	2.0	XXVIII	1.4	XXIX	1.0	III
	Cl^-	2.0	XXXIII	1.4	XXXIV		
	$SO_4^=$			2.0 → 0	XXXV		
DBM	ClO_4^-	2.0	XL	1.3	XLI	1.0	I
TA	ClO_4^-	2.0	XLV	1.5	XLVI	1.0	III
MeTTA	ClO_4^-			2.0	XLIV	1.0	VII

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TABLE V

LEAST SQUARES ANALYSIS OF PLOTS LOG D VS. VARIANT

	Variant - (HT)			Variant (S)	Variant - pH		
β-Diketone	No S	S	Medium	ClO_4^-	No S	S	Medium
BTA	2.0	2.1	ClO_4^-	1.0	1.0	1.9	ClO_4^-
	2.0		NO_3^-		1.9		NO_3^-
FTA	2.0	1.8	ClO_4^-	0.9	1.5	1.8	ClO_4^-
TTA	1.9	2.0	ClO_4^-	0.9	1.8	2.0	ClO_4^-
					1.9	2.0	Cl^-
AA	2.2	1.8	ClO_4^-	0.9	1.8	1.4	ClO_4^-
		1.8	$SO_4^=$				
BA	2.2	1.9	ClO_4^-	0.9	1.8	1.4	ClO_4^-
					2.0	1.4	Cl^-
DBM	2.2	1.8	ClO_4^-	1.0	2.0	1.3	ClO_4^-
TA	1.8	1.9	ClO_4^-	0.9	2.0	1.5	ClO_4^-
MeTTA		1.8	ClO_4^-	1.2		1.8	ClO_4^-

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TABLE VI

LOGARITHMS OF EQUILIBRIUM CONSTANTS .

β-Diketone	Log K_t	Log K_{ts}	Log K_s	pK_D [a]
FTA	-2.25	2.74	4.99	8.50
TTA	-2.41	2.61	5.02	9.10
BTA	-2.90	2.41	5.31	9.20
TA	-4.68	-1.44	3.24	12.35
AA	-5.81	-2.25	3.56	12.70
BA	-5.42	-1.52	3.90	12.85
DBM	-5.52	-1.10	4.42	13.75

[a] reference 29.

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TABLE VII

VALUES OF LOG K_{ts}

β-Diketone	Variant - (HT)	Variant - (S)	Variant - pH
FTA	2.74	2.96	2.59
TTA	2.61	2.71	2.43
BTA	2.41	2.46	2.27
TA	-1.44	-1.17	
AA	-2.25	-2.19	
BA	-1.52	-1.59	
DBM	-1.10	-1.25	
MeTTA	-3.09	-2.21	-2.95

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TABLE VIII

VALUES OF LOG K_t

β-Diketone	Variant - (HT)	Variant - pH
TTA	-2.41	-1.99
TA	-4.68	-4.58
AA	-5.81	-5.21
BA	-5.42	-5.04
DBM	-5.52	-5.51

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TABLE IX

DIFFERENCES IN EXTRACTION AND ENHANCEMENT

β-Diketone	Δlog K_t	Δlog K_{ts}	Δlog K_s
AA	0.00	0.00	0.00
BA	0.39	0.73	0.34
DBM	0.29	1.15	0.86
TA	1.13	0.81	-0.32
BTA	2.91	4.66	1.75
TTA	3.40	4.86	1.46
FTA	3.56	4.99	1.43

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DISCUSSION

SYSTEMS INVESTIGATED.

Systems involving the following β-diketones have been investigated: thenoyltrifluoroacetone (TTA), furoyltrifluoroacetone (FTA), benzoyltrifluoroacetone (BTA), thenoylacetone (TA), benzoylacetone (BA), dibenzoylmethane (DBM), acetylacetone (AA), and 4,4,4-trifluoro-2-methyl-1-(2-thienyl)-1,3-butanedione (MeTTA).

TTA was investigated because it is the most widely used β-diketone for the extraction of the actinide and lanthanide ions studied by other investigators. A comparison of K_t, K_s and K_{ts} for the uranyl-TTA-TBP system was made between the results of this work and of previous work. A study of the other β-diketone systems followed.

Since the studies of synergic systems had been limited to the use of TTA as β-diketone, a study of FTA and BTA was undertaken to determine if the thienyl group was a necessity in the structure for synergism to occur. A preliminary report[30] from Brookhaven National Laboratory stated that the trifluoromethyl group was a necessary structural entity in the β-diketone for the synergic phenomenon to occur. However, the work of Szábo showed synergism in the uranyl-AA-TBP system. BA and TA were studied for direct comparison with BTA and TTA respectively. AA was investigated to check the results of Szábo, for he could not fully explain his findings.

Dibenzoylmethane, another common chelating agent, is employed in extraction procedures involving metal ions.[31] This β-diketone was studied to determine the effect of the symmetrical structure, as opposed to those of BA and BTA. The two phenyl groups could also lead to steric

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effects if the synergist were to bond to the chelated β-diketone or to the metal.

The aforementioned β-diketones contained R-groups significantly different from one another in order to demonstrate whether a specific R-group was a necessary requisite for synergism to occur, either by direct interaction of the group with TBP or through electronic factors, such as a change in acidity. There remained only one position on the β-diketone which had not been altered, the carbon atom between the two ketone groups. The hydrogen bonded to the center carbon on the β-diketone could not be considered to be acidic, but there was a possibility that the unalkylated oxygen in TBP could interact at this position. In order to check on this possibility, a study of MeTTA was undertaken. One hydrogen on the middle carbon is replaced by a methyl group in this compound. If an enhancement of extraction was evident with MeTTA, this position could be eliminated as a site for addition of TBP to the chelated β-diketone.

The work of Healy[10,11] had previously ruled out interaction of TBP with the ketohydrate form of the β-diketone as discussed below and so all possible sites for interaction have been structurally altered.

METAL-TBP BOND.

Newman[12] proposed that TBP interacts with the chelated β-diketone because K_s values for TTA did not change for a series of metal ions. Healy and Ferraro[10,11] presented infrared evidence to show that one β-diketone ligand becomes monodentate and concluded that TBP hydrogen bonds to the free enolic hydroxyl group. They had assigned the peak about 1600 cm^{-1} to the metal-carbonyl vibration. They claimed that

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insertion of a neutral organophosphorus compound in metal-TTA complexes caused this single peak to split into two peaks, indicating that some TTA carbonyl was becoming free. Li[32] performed the same infrared experiments and found that in some metal-TTA complexes, the bond at 1600 cm^{-1} is split before TBP is added and therefore the assignment of bonds in these spectra is uncertain.

Healy[10,11] ruled out interaction of the ketohydrate form of the β-diketone with TBP because complexation increased as the concentration of water decreased in the organic diluent and no ketohydrate spectrum was found. His conclusion is supported by the fact that the extraction of uranyl ion with AA was synergically enhanced by TBP although AA does not exhibit a ketohydrate structure. Therefore synergism cannot be due to the interaction of TBP with a ketohydrate hydroxyl group.

The extraction of uranyl ion was synergically enhanced by TBP with all the β-diketones studied. While there is no direct proof that TBP is bonded to the metal ion, it is apparent that no one functional group on the chelated β-diketone can be involved in the bonding. This fact coupled with the aforementioned evidence leads to the conclusion that TBP does not interact with the coordinated β-diketone, but instead probably bonds directly to the metal. If metal bonding is involved then it appears that uranium is at least seven coordinate. That the coordination number of uranium(VI) can rise to eight has been established by x-ray crystallography for the triple acetate, $Na[UO_2(C_2H_3O_2)_3]$ [33] and for the complex $UO_2(NO_3)_2 \cdot 2(C_2H_5O)_3PO$.[34] However, while the studies of Sacconi[35] of the infrared spectra of complexes of uranium(VI) with β-diketones have provided abundant evidence that these complexes are coordinately unsaturated, it appears that they generally form adducts

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with only one molecule of water, ammonia, pyridine, etc., and that this molecule is coordinated directly to the central metal atom thus producing seven coordinate uranium. The failure to form eight coordinated complexes in these cases may be due to steric factors which would be even more pronounced with TBP.

EXPLANATION OF SYNERGIC BEHAVIOR.

If metal bonding is involved, TBP most probably replaces a water molecule from a coordination site on the metal. This replacement renders the complex less hydrophilic and more soluble in the organic phase. Healy[9] isolated the water insoluble crystalline yellow uranyl-TTA-TBP solid complexes with approximately the expected metal-TTA-TBP mole ratios which contained practically no water. He also studied synergic effects in various organic diluents[36], a study which pointed out that as the solubility of water decreases in a series of diluents the synergic effects increase. The solubility of a series of uranyl-β-diketone-aquo complexes should decrease in the organic diluent as water decreases in solubility therein. The replacement of a water molecule with TBP greatly increases the solubility of the complex in the organic phase. However, the greater the solubility of the aquo complex in the organic phase initially, the less the degree of enhancement.

The equation for the organic phase reaction may be written as

$$UO_2T_2(H_2O)_y + y\ TBP \rightleftharpoons UO_2T_2(TBP)_y + y\ H_2O$$

where K_s is the equilibrium constant associated with this reaction.

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INTERPRETATION OF GRAPHS.

In order to establish which of the β-diketones studied is the best extractant, it was necessary to normalize the graphs of log (D_s-D_o) vs. log (TBP). The extraction studies were carried out at either pH = 1.0 or pH = 3.0 depending on the acidity of the β-diketones. Since the pH of the system affects the extracting ability of the β-diketone it was necessary to incorporate a pH factor in plotting the data points. This was accomplished by plotting log (D_s-D_o) - 2 pH vs. log (TBP) . The best straight lines that can be drawn through the data points of these graphs have slopes of one. (Figures I - VII). As the concentration of TBP increases, negative deviations from the slope of one appear. The decrease of the values of the gradient is probably due to the increasing tendency for the two solutes (β-diketone and TBP) to associate. Such association, which was confirmed by infrared measurements made by Healy[10], will decrease their effective individual concentrations. Healy attributed the association to hydrogen bonding between TBP and the enolic form of the β-diketone.

A comparison between MeTTA and the other β-diketones shows that MeTTA is the weakest ligand in acid solution in the presence of synergist, probably due to its high pK_D caused by the replacement of an enolic hydrogen with a methyl group.

THORIUM - MeTTA.

Healy[5] postulated that a mechanism for the synergic extraction of thorium would necessarily be different than the mechanism in the uranyl system since he thought ThT_4 to be coordinately saturated. He postulated addition of TBP to the chelated β-diketone. Work with

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trioctylamine led Newman[7] to conclude that the amine hydrochloride added to the β-diketone in the thorium system. It was of interest to study the thorium-MeTTA-TBP system to see if TBP would interact with MeTTA. Earlier work in this investigation leads to the conclusion that all sites for interaction of TBP on the chelated MeTTA are thought to be ruled out. If an interaction occurs in this system the TBP may be bonding directly to thorium. The slope of the graph of log (D_s-D_o) - 2 pH vs. log (TBP) for this thorium system was 1.0 (Figure VI). If TBP adds directly to the thorium atom then the coordination number would increase to a value greater than eight. Ten-coordinate thorium structures have been proposed by Bohigian and Martell[37] for the thorium derivative of triethylenetetraminehexaacetic acid, by Goldstein, Menis and Manning[38] for a bis(acetic acid) complex of tetrakis(thenoyltrifluoroaceto) thorium, and by Meutterties[39] for a pentakis(tropolono)-thorium complex. Thus the mechanism for the synergic extraction of thorium may be the same as that of uranium.

Further examination of the plot of log (D_s-D_o) - 2 pH vs. log (TBP) for the thorium system shows that deviations from a slope of 1.0 were obtained for TBP concentrations greater than 0.016 M. This deviation is more pronounced than in the uranyl system because the concentration of the β-diketone in this case is raised to the fourth power in the expression for D_s since ThT_4 is formed. With the assumption that a one to one compound is formed a value of log K = 0.23 for the interaction of MeTTA with TBP was calculated from this deviation. Log K_{ts} was obtained by evaluating the intercept of the line with a slope of 1.0 in Figure VI assuming the concentration of HT to be 0.2 M. This value was then substituted into the equation for the intercept;

$$\log K_{ts}\,(HT)^4\,[H^+]^{-4} = \text{Intercept}$$

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and free (HT) evaluated for the deviated line. The concentration of HTS is obtained as follows

$$(HTS) = (HT)_{total} - (HT)_{free}$$

Free (S) is obtained by subtracting (HTS) from 1.0, the value of total (S) at the intercept of the graph. The three calculated values are substituted into the following equation

$$K = \frac{(HTS)}{(HT)\ (S)}$$

and K evaluated.

pH AS VARIANT.

Theoretically, another means of obtaining the number of molecules of β-diketone that coordinate to the metal ion would be to obtain the slope of a graph of log D_o vs. pH or log D vs. pH, applying equations (6) and (10) respectively. This approach was investigated and large deviations from slope 2.0 were obtained for BTA and FTA in the absence of synergist and for AA, BA, DBM and TA (so-called weakly acidic β-diketones) in the presence of synergist. These deviations might have been attributed to the formation of aqueous complexes, such as UO_2T^+ in the absence of synergist and UO_2TS^+ in the presence of synergist. The following experiments show that these suppositions are incorrect. Extraction studies were performed using an aqueous complexing solution so that the anion present would eliminate the formation of aqueous β-diketone complexes. A sodium nitrate solution was chosen for these studies in the absence of synergist, but nitrate ion forms substitution complexes[2] with β-diketones in the presence of synergist

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so a potassium sulfate solution was used in the presence of TBP. All extraction studies carried out in nitrate or sulfate media had lower log D_o and log D values than the comparable experiments in perchlorate solution. The slopes of the plots of log D_o vs. pH and log D_o vs. log (HT) for BTA in a nitrate medium were 2.0 (Figure XIV and XXXVIII). It has been shown that the slope of the plot of log D_o vs. log (BTA) is 2.0 in perchlorate medium, (Figure XXIII), hence no satisfactory explanation on the basis of aqueous complexes can account for the slope deviations. If UO_2T^+ were formed in perchlorate solution then the slope of the plot of log D_o vs. log (BTA) should also deviate from 2.0. If UO_2T_2HT were formed from UO_2T^+ then the slope in nitrate medium should be greater than 2.0. This same type of argument was used to disprove the existence of aqueous complexes in the presence of synergist; the slope of the plot of log D vs. pH for AA in a sulfate medium was 2.0 as was the plot of log D vs. log (AA) (Figures X and XXVII).

The work in sulfate medium was extended to BA and TTA. In these cases the slopes were not 2.0. The plot for BA showed a slope of 2.0 from a pH of 1.2 to 1.8 and then a gradual decrease until a slope of 0.0 was obtained approximately pH 2.3 (Figure XXXV). The plot for TTA showed a slope of 1.3 from a pH of 0.8-1.8 with a gradual decrease to a slope of 0.0 about pH 2.1 (Figure LI). These observations may be explained by the following series of competitive reactions:

$$UO_2(SO_4)_3^{4-} + 2\ HT + S \rightleftharpoons UO_2T_2S + 3\ SO_4^{=} + 2\ H^+$$

$$UO_2T(SO_4)_2^{3-} + HT + S \rightleftharpoons UO_2T_2S + 2\ SO_4^{=} + H^+$$

$$UO_2T_2SO_4^{=} + S \rightleftharpoons UO_2T_2S + SO_4^{=}$$

AA is not able to form aqueous mixed complexes with sulfate in

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the pH range investigated. The distribution involves the aqueous sulfate complex $UO_2(SO_4)_3^{4-}$ and the complex in the organic phase UO_2T_2S. Ahrland[40] has studied the uranyl-sulfate system and obtained formation constants corrected to zero ionic strength, log K_1 = 2.93, log K_2 = 0.85 and log K_3 = -0.38. Log K_t and log K_{ts} for AA have the lowest values for the β-diketones studied, which supports the observation that AA does not compete well with sulfate for the uranyl ion. BA has higher values for log K_t and log K_{ts}, and as the pH increases the competition for the metal ion between BA and $SO_4^{=}$ increases. Mixed aqueous complexes are formed. At pH values below 1.6 the equilibrium reaction involves $UO_2(SO_4)_3^{4-}$ and UO_2T_2S. As the pH increases $UO_2T(SO_4)_2^{3-}$ forms and the slope deviates from 2.0. Finally at high pH values the β-diketone can replace two sulfate ions in the coordination sphere in the aqueous phase and a slope of 0.0 is obtained because of the equilibrium reaction involving $UO_2T_2SO_4^{=}$ and UO_2T_2S. TTA competes so well with sulfate that mixed complexes are present in the entire pH range studied and the slope is never as great as 2.0. The formation of $UO_2T_2SO_4^{=}$ occurs at lower pH and a slope of 0.0 is obtained earlier than with BA.

KINETIC STUDIES.

No reasonable species in either phase could explain deviations from theoretical slope values in a non-complexing medium. Theoretically proper slopes were obtained in complexing media, which disproved the supposition that UO_2T^+ and UO_2TS^+ were forming in perchlorate solution. If these species were formed slopes of 2.0 could not be obtained in complexing and non-complexing media when variant was β-diketone.

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A kinetic study with pH as variant (appendix, pp.91-95) revealed that the deviations from a slope of 2.0 in perchlorate or chloride are due to the formation of a species which is extracted at a low rate. This reaction did not attain equilibrium in the elapsed time of an experimental run.

Data collected from these experiments showed that high D values were obtained before acid was added to the system and the system was at equilibrium. After the addition of acid the D values were lower but as time increased, at constant pH, the D values increased.

The first step in the experimental procedure is an extraction of the uranyl ion from the aqueous to organic phase. The extraction of uranyl ion proceeds at a fast rate and the system is at equilibrium within the forty minute interval allotted in the experimental procedure, as shown in the appendix (pp.91-95). The succeeding steps involve the addition of 2.0 M perchloric acid, which should strip uranyl ion out of the organic phase. Uranium is stripped into the aqueous phase and is re-extracted at a low rate. This low rate caused the slope of the plot of apparent log D_o vs. pH in previous experiments to deviate from 2.0. It seems possible that perchlorate or chloride would be bonded to this species since the effect occurs only with these anions. The kinetic experiments carried out with BTA and FTA (pp.92-94) showed that variation in waiting time of approximately 100 minutes had as much effect as a unit change in pH. Log D_o values of the first extraction step in the kinetic experiments were approximately the same as those of similar systems where pH was varied.

This same general explanation may hold for the extraction of the weakly acidic β-diketones in the presence of TBP, when perchloric or

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hydrochloric acid is added to strip the organic phase of uranyl ion. In these systems however, the species formed after stripping would contain bonded TBP, as is evident from the fact that this type of extraction does not occur in the absence of TBP with these β-diketones. Experiments carried out with BA in several constant TBP concentrations as pH was varied showed that as the TBP concentration was lowered the slope deviations from 2.0 became smaller. Kinetic experiments with AA in the presence of TBP showed that the first extraction step proceeded at a fast rate. Log D values of the first extraction step in the kinetic experiments were approximately the same as those of similar systems where pH was varied.

In order to insure that a slope of 2.0 meant that stripping was not followed by extraction of metal ion at a low rate, a kinetic experiment involving BTA and TBP was carried out (p. 95). The results showed that equilibrium was rapidly achieved. Values of log D agreed within experimental error with those obtained in experiments in which pH was variant (p. 83). In both cases the value of the slope was 2.0.

The results of Szábo[13] show deviations from slope 2.0 for AA in perchloric acid, in agreement with the findings of this work. Szábo tried to explain the deviation as being caused by the formation of $UO_2T(HT)S(ClO_4)$. The deviations, however, are probably caused by the aforementioned kinetic effect.

ATTAINMENT OF EQUILIBRIUM.

The systems studied where the experimental procedure did not involve addition of acid were at equilibrium. This fact was shown by raising and lowering the concentration of solute by addition of solute

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in diluent or diluent alone. Log D values obtained in this manner were the same whether the concentration of solute was obtained by adding solute or diluting a higher concentration of solute. The plots of log (D_s-D_o) vs. log (TBP) were compared with those of log D vs. pH for BTA, FTA and TTA. Log D values on each set of plots were the same where the β-diketone concentration was equal to 0.2 M, the TBP concentration was equal to 0.2 M and the pH values were equal.

EQUILIBRIUM CONSTANTS.

The values of the equilibrium constants obtained for TTA agree reasonably with literature values.

	K_t	K_{ts}	K_s	Medium
Irving & Edgington[4]	-2.8			0.01 M nitrate
Walton[40]	-2.5			0.01 M nitrate
Newman[12]	-2.26	4.70	2.48	2.0 M chloride
This work	-2.41	5.02	2.61	2.0 M perchlorate

The differences may be attributed to the changes in aqueous media and the differences in experimental error in the analysis of uranium by counting techniques or fluorimetry. The only other literature data available, obtained by Stary and Hladsky[41], were values of log K_t for BA and DBM in 0.1 M sodium perchlorate of -4.68 and -4.12 respectively. These values disagree with the work in this paper, which may be due to the experimental method employed. Stary obtained data by varying pH with additions of 0.1 M sodium hydroxide to the aqueous phase. Strong base is known to cleave β-diketones thereby forming acid and ketone. These species either alone or in combination could affect the extraction.

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The authors mention slow attainment of equilibrium in the systems they studied and perhaps a similar kinetic effect to the one found in this work was operative.

LOG K_t.

An examination of the graph of log K_t vs. pK_D (p. 43), where K_D is the dissociation constant of the β-diketone, shows that the degree of extraction of uranyl ion by a β-diketone depends on the acid strength and the structure of the β-diketone. The values of log K_t increase as pK_D decreases with the exception of AA. Since this system involves a heterogeneous equilibrium the structure of the β-diketone should affect the extraction of metal ion. If pK_D values are the same for two β-diketones the β-diketone with a structure closer to that of the diluent should extract to a greater degree. This expectation is borne out by a comparison of AA and the other β-diketones. Log K_t is much lower for AA because the substitution of a methyl group for an aromatic group more than offsets the acidity of AA. This discussion of the interplay of structure and acidity may be extended to a comparison of BTA and BA. Because of its electron withdrawing properties the trifluoromethyl group causes the acid strength of a β-diketone to increase. The difference in pK_D between BA and BTA is 3.65 units and BTA has a log K_t value 2.5 units greater than BA.

Values of log K_t obtained by different methods (Table VIII) agree reasonably well in most cases, with exceptional agreement in the cases of TA and DBM. This provides further proof that kinetic effects are not present in systems involving β-diketones listed in Table VIII,

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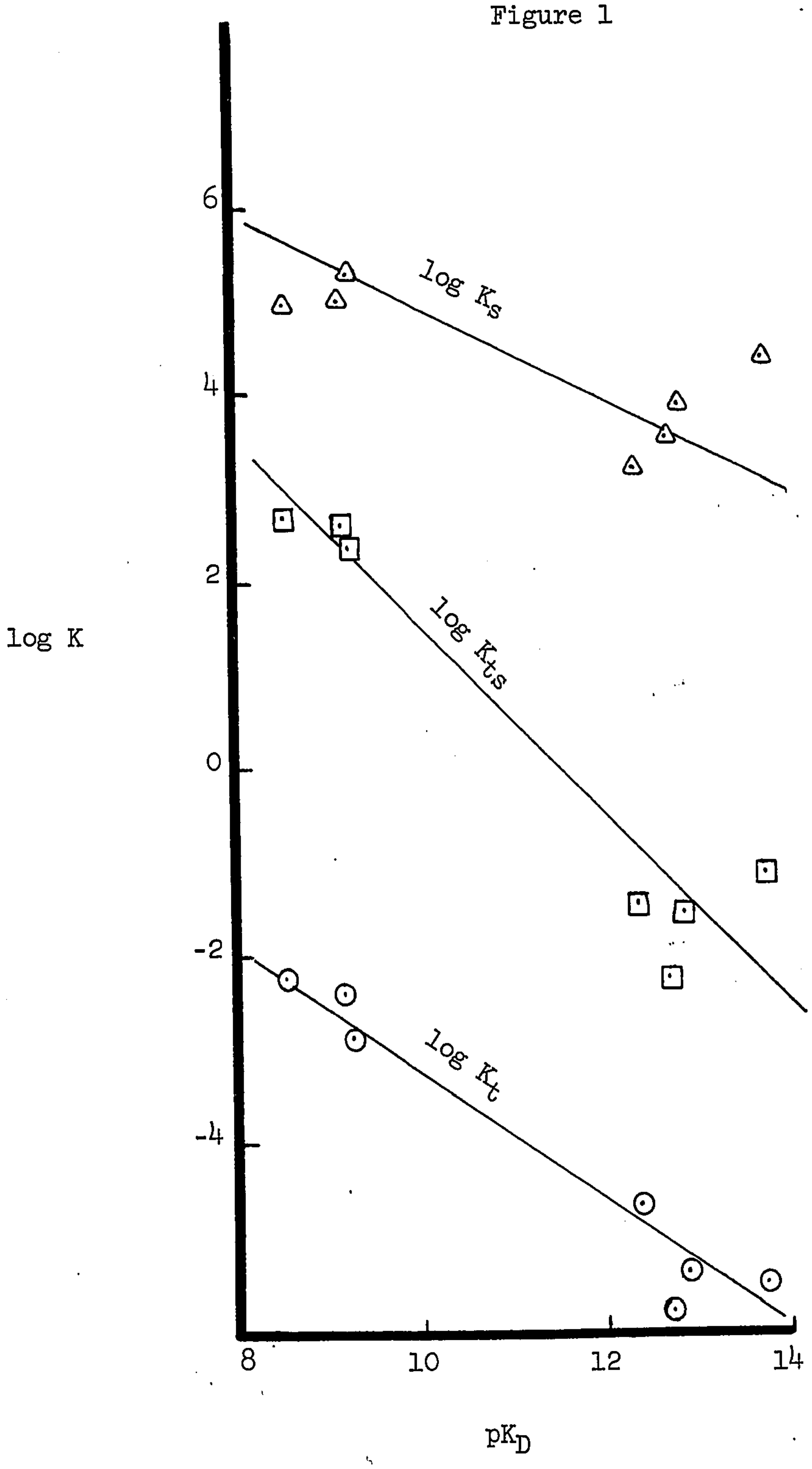
Figure 1



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LOG K_s.

The sigma bond strength of the metal-β-diketone bond increases as pK_D of the β-diketone increases.[43] Comparisons of different β-diketones are possible since the systems are similar. An analysis of log K_s values for the weakly acidic or strongly acidic β-diketones shows that an increase in sigma bond strength is accompanied by an increase in the ability of TBP to bond to uranium. As the sigma bond strength increases in these complexes the pi bonding must increase thereby reducing the increased negative charge on the metal atom. The metal electrons are made available for donation to ligand orbitals and this back donation actually decreases the negative charge on the metal thereby increasing the degree of sigma bonding with the TBP oxygen. Although the introduction of a trifluoromethyl group decreases the sigma bond strength of the metal-β-diketone bond, the degree of pi bonding is greatly enhanced by the attraction by the trifluoromethyl group of the pi cloud of the aromatic chelate system thereby permitting the metal to donate more electronic charge into this pi system. This effect greatly outweighs the reduction in sigma bond strength of the metal β-diketone bond. See Table VI and Figure 1.

LOG K_{ts}.

Values of log K_{ts} obtained from all the solvent extraction methods employed in this work, where applicable, are compared in Table VIII. Excellent agreement is obtained within experimental error for the three methods, aside from MeTTA. In the latter case the value of log K_{ts}, Variant - (S), is lower than the values obtained from the other methods. MeTTA data gave the poorest fit for a slope of 1.0 when TBP

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was varied and this may explain the discrepancy.

The order of synergic extraction for the β-diketones remains the same for each method employed with the exception of TA and DBM. Although the difference between FTA and TTA within each set of data is not meaningful, it appears that FTA is a better extractant in the presence of TBP because its log K_{ts} value is the higher for each method employed. From these data and Figure 1 it appears that log K_{ts} is proportional to pK_D.

ENHANCEMENT OF EXTRACTION.

The differences in enhancement for the β-diketones studied point out the variation in the degree of pi bonding between the strongly acidic and weakly acidic β-diketones and within each group (Table IX). It must be pointed out that the differences in enhancement between the β-diketones are not as great as the differences in extraction in the absence of synergist (Δ log K_t). The differences in enhancement are due to the indirect effects on the metal-TBP bond caused by the other ligands rather than direct electronic effects on the metal-ligand bonds in the β-diketone chelation to the metal. The greatest difference in enhancement values (Δ log K_s) is 2.07, while the greatest difference in extraction in the absence of synergist (Δ log K_t) is 3.56.

URANYL - MeTTA.

Extraction in the presence of synergist combines the chelation of the metal by β-diketone molecules and coordination of the metal by TBP. Log K_{ts} values should reflect both types of bonding. The

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value of log K_{ts} was calculated for uranyl-MeTTA and found to be -3.09. A comparison can be made concerning β-diketone chelation in each system if one considers MeTTA bonding to contribute much more to the value of the constant than the TBP bonding, which is true for the other β-diketones studied. The replacement by a methyl group of an enolic hydrogen in TTA has the effect of markedly lowering the acidity. The organic nature of the methyl group should increase the extractability of the complex but this is greatly offset by the decrease in acidity. The difference in log K_{ts} values for TTA and MeTTA is 5.70, which demonstrates that acidity of the β-diketones plays the major role in the extraction of metal ions both in the presence and absence of synergist.

IMPROVEMENT OF EXTRACTION.

An analysis of plots of log K_s, log K_{ts}, and log K_t vs. pK_D (Figure 1) shows that a linear dependence is evident for all three plots but a first power dependency is found for log K_{ts} vs. pK_D. This dependency in itself is important since the other two plots have values of slopes less than one. The change in structure of the β-diketones caused solubility effects as well as steric factors to play a role in these systems. However, the addition of TBP permits the acid strength of the β-diketone to play its full role in affecting the bonding, and log K_{ts} is directly proportional to pK_D with unit slope. This enhancement of acid strength may be a secondary effect in the synergic phenomenon.

Use of these plots permits the semi-quantitative estimation of log K_{ts}, log K_t and log K_s if the pK_D value is known.

The practical aspect of this problem is approached through

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log K_{ts} and $\Delta \log K_{ts}$ values. It appears that of all the β-diketones studied, FTA is the best extractant of uranium in the presence of TBP. It is also the strongest acid. Seemingly, the optimum β-diketone for extraction of uranyl ion should have as low a pK_D as is compatible with terminal R-groups similar in structure to that of the organic diluent.

CONCLUSIONS.

Thus it seems that any system containing a β-diketone and TBP will synergically extract uranium. TBP probably coordinates directly to the central metal atom replacing a molecule of water in the coordination sphere. Uranium is at least seven-coordinate in the complex. The replacement of a water molecule by TBP causes this complex to be less hydrophilic and more soluble in benzene enabling more chelated uranium to enter the organic phase.

Analysis of the equilibrium constants has shown that synergic extraction of uranium increases as the acid strength of the β-diketone increases and the degree of dative pi bonding of the metal-β-diketone bond increases. The difference in acid strength plays a more important role in this system and it would appear that the use of β-diketones with low pK_D values will insure the greatest degree of synergic extraction in acid media.

These criteria can be extended to the extraction of any metal that is coordinately unsaturated. The work with thorium shows that much is to be learned about maximum coordination number of the metals.

Finally, it may be noted through experiences in this work and the work of Stáry[41] and Szábo[13] that reliable data cannot be obtained in solvent extraction of metals with certain β-diketones if either

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strong acid or base is added to the system to change pH. Decomposition of β-diketones may occur and many side reactions can follow.

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FURTHER STUDIES

It has been demonstrated that synergic enhancement is probably due to the replacement of a water molecule by TBP in the coordination sphere of the metal. Healy[10] was able to isolate a solid uranyl-TTA-TBP complex. If a single crystal of this synergic complex could be obtained it would be of interest to subject it to x-ray analysis to determine its structure. This would confirm the presence of a metal-TBP bond.

A nuclear magnetic resonance study of ^{31}P may also aid in furnishing additional confirmatory evidence for metal-TBP bonding. The isomer shift of ^{31}P will be greater if TBP is bonded to uranium rather than interacting with a chelated β-diketone.

Synthesis of β-diketones with high acid strength should be attempted. Electron withdrawing groups on a phenyl ring would increase the acid properties of a β-diketone and would be an excellent extractant in the presence of synergist. Other β-diketones such as 4,4,4-trifluoro-1-(2-pyridinyl)-1,3-butanedione would have high acid strength and yet would enhance the degree of pi bonding with the metal ion. Hexafluoroacetylacetone would have a greatly increased acid strength and would probably extract markedly in the presence of TBP. However, this β-diketone is markedly soluble in water and this factor would have to be assessed. Synthesis of monofluoromethyl or difluoromethyl substituted TA should be attempted to obtain a β-diketone with a pK_D value in the range of 11. Values of log K_t and log K_{ts} could be obtained for this β-diketone and an assessment made of the use of Figure 1 to semiquantitatively estimate these values.

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Finally it would be of interest to see if synergic phenomena are present in systems containing coordinately unsaturated transition metals. A study of "coordinately saturated" metal β-diketonates could possibly lead to conclusions as to how much is really known about the bonding in metal chelates.

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SUMMARY

Extraction studies were carried out with acetylacetone, benzoylacetone, benzoyltrifluoroacetone, dibenzoylmethane, furoyltrifluoroacetone, thenoylacetone, thenoyltrifluoroacetone and 4,4,4-trifluoro-2-methyl-1-(2-thienyl)-1,3-butanedione in the presence of tributyl phosphate as synergist to determine the conditions necessary for obtaining and improving synergic enhancement of the solvent extraction of uranium, the nature of the synergic complex, and how the synergic agent is bonded in this complex. The above β-diketones were chosen so that all possible sites for bonding of the synergist with the β-diketone would be varied. Synergic enhancement occurred in all cases proving that the synergist could not bond to the β-diketone. It was concluded that TBP probably bonds directly to uranium. This conclusion coupled with the work of Healy[5,36] concerning the effect of various organic diluents on enhancement of extraction and solubility studies of $UO_2T_2(H_2O)_x$ in these diluents leads to the following equation for the explanation of the synergic phenomenon:

$$UO_2T_2(H_2O)_x + x\ S \rightleftharpoons UO_2T_2S_x + x\ H_2O$$

The most common extracted species is generally represented by UO_2T_2S. This species is rendered less hydrophilic with the replacement of a water molecule by TBP and is more soluble in the organic phase.

Equilibrium constants for the following reactions were obtained for all the aforementioned β-diketones. The stoichiometries of the extracted complexes for all the β-diketones were also obtained and are

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represented by the species below.

$$UO_2^{2+} + 2\ HT \rightleftharpoons UO_2T_2 + 2\ H^+ \qquad K_t$$

$$UO_2^{2+} + 2\ HT + S \rightleftharpoons UO_2T_2S + 2\ H^+ \qquad K_{ts}$$

$$UO_2T_2 + S \rightleftharpoons UO_2T_2S \qquad K_s$$

Interpretation of the values of these equilibrium constants led to the conclusion that the extraction of uranium by any β-diketone should be enhanced by the addition of TBP. The synergic extraction of uranium varies directly with the acid strength of the β-diketone and with the degree of pi bonding between the metal and the β-diketone. FTA, the strongest acid, showed the highest value for K_t while BTA exhibited the highest value for K_s. BTA forms a stronger sigma bond with uranium and the metal is able to reinforce the degree of pi bonding with BTA to a greater degree than with FTA. However, the acid strength of the β-diketone plays the major role in the synergic extraction of uranium as is evidenced from values of K_t and K_{ts}. Improvement of the extraction of uranium in the presence of TBP may be brought about by choosing a β-diketone with a low pK_D value containing terminal R-groups capable of increasing the degree of pi bonding with uranium.

A semiquantitative method was developed for estimating K_t, K_s, and K_{ts} for a β-diketone once pK_D is known by application of a plot of log K_t, log K_s and log K_{ts} vs. pK_D (Figure 1, p. 43). The values of these equilibrium constants may be read directly from this graph.

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APPENDIX

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APPENDIX

DATA.

The experimental data are collected on pages 55 through 95. Symbols are defined on pages iv and v. All extractions were performed in 2.0 M lithium perchlorate unless stated otherwise. Extractions employing salts other than lithium perchlorate contained aqueous media of ionic strength 2.0.

The figures are collected on pages 96 through 146. Corresponding data appear on the pages indicated in The List of Figures, pages ix-xi.

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AA - UO_2^{2+} - TBP Variant - TBP (0.987 M)

pH = 2.50 D_o = 0.022

d_b	d_a	log (D_s-D_o)	V	log [TBP]
3.2	73	-1.670	0.05	-3.006
5.0	73	-1.336	0.10	-2.701
9.1	71	-0.975	0.20	-2.398
16	71	-0.692	0.40	-2.087
24	59	-0.415	0.70	-1.836
32	55	-0.252	1.00	-1.682
38	48	-0.114	1.40	-1.533
42	43	-0.020	1.90	-1.398
48	39	0.082	2.40	-1.295
34	34	-0.010	3.20	-1.170
50	29	0.231	4.30	-1.044
52	24	0.331	6.00	-0.906
57	19	0.474	7.60	-0.602
46	17	0.429	9.30	-0.558
48	16	0.474	*	-0.644
38	17	0.345	*	-0.718

* 10.00 ml of 0.20 M AA added

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AA - UO_2^{2+} - $SO_4^{=}$ - TBP Variant - TBP (0.994 M)

pH = 2.30 D_o = 0.003

d_b	d_a	log (D_s-D_o)	V	log [TBP]
0.63	110	-2.620	0.05	-3.003
1.0	110	-2.237	0.10	-2.699
1.6	100	-1.896	0.20	-2.391
3.0	96	-1.553	0.40	-2.084
5.0	100	-1.331	0.70	-1.837
6.6	96	-1.184	1.00	-1.679
10	96	-0.996	1.40	-1.530
13	87	-0.835	1.90	-1.395
16	87	-0.743	2.40	-1.292
20	85	-0.634	3.20	-1.167
25	80	-0.510	4.30	-1.041
27	71	-0.424	6.80	-0.825
36	60	-0.224	9.30	-0.707

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BA - UO_2^{2+}- TBP   Variant - TBP (0.987 M)

pH = 2.40 D_o = 0.024

d_b	d_a	log $(D_s - D_o)$	V	log [TBP]
6.6	77	-1.212	0.05	-3.006
13	71	-0.799	0.10	-2.701
20	62	-0.525	0.20	-2.398
33	54	-0.231	0.40	-2.087
38	48	-0.115	0.70	-1.836
43	44	-0.021	1.00	-1.682
49	38	0.120	1.40	-1.533
56	31	0.251	1.90	-1.398
59	25	0.369	2.40	-1.295
67	17	0.593	3.20	-1.170
61	13	0.669	4.30	-1.044
70	8.7	0.904	6.01	-0.906
67	6.5	1.012	7.60	-0.602
71	5.2	1.135	9.30	-0.558
57	5.4	1.022	*	-0.644
45	4.7	0.980	*	-0.718

* 10.00 ml of 0.20 M BA added

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BTA - UO_2^{2+} - TBP Variant - TBP (0.987 M)

pH = 1.20 D_o = 0.038

d_b	d_a	log (D_s-D_o)	V	log [TBP]
57	24	0.369	0.05	-3.006
68	14	0.683	0.10	-2.701
64	8.0	0.901	0.20	-2.398
74	3.7	1.300	0.40	-2.087
82	1.9	1.635	0.70	-1.831
80	1.2	1.824	1.00	-1.682
82	0.71	2.063	1.90	-1.398
78	0.60	2.114	2.40	-1.295
77	0.43	2.253	3.20	-1.170
74	0.29	2.407	4.30	-1.044
70	0.20	2.544	6.00	-0.906
71	0.21	2.529	7.60	-0.602
72	0.16	2.653	9.30	-0.558
58	0.14	2.617	*	-0.644
49	0.13	2.576	*	-0.718

* 10.00 ml of 0.20 M BTA added

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DBM - UO_2^{2+} - TBP   Variant - TBP (0.987 M)

pH = 2.44 D_o = 0.016

d_b	d_a	log (D_s-D_o)	V*	log [TBP]
30	45	-0.186	0.10	-2.404
49	31	0.195	0.25	-2.002
61	21	0.461	0.40	-1.784
62	16	0.587	0.60	-1.608
56	12	0.668	0.85	-1.455
68	8.6	0.897	1.20	-1.303
59	6.8	0.938	1.80	-1.207
67	5.4	1.093	2.40	-1.129
68	4.8	1.151	3.20	-1.044
60	3.3	1.259	4.00	-0.973
60	3.0	1.301	5.00	-0.908
58	2.3	1.401	6.20	-0.834
57	1.6	1.552	8.20	-0.737
52	1.1	1.673	11.40	-0.627
52	1.2	1.635	**	-0.710
38	1.3	1.466	**	-0.774

* first six additions were 1.974 M in TBP

** 10.00 ml of 0.20 M DBM added.

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FTA - UO_2^{2+} - TBP   Variant - TBP (0.987 M)

pH = 1.21 D_o = 0.588

d_b	d_a	log (D_s-D_o)	V	log [TBP]
72	9.0	0.870	0.05	-3.006
73	3.9	1.258	0.10	-2.701
78	1.8	1.631	0.20	-2.398
87	0.95	1.959	0.40	-2.087
84	0.52	2.212	0.70	-1.836
82	0.38	2.333	1.00	-1.682
88	0.25	2.546	1.40	-1.533
69	0.17	2.608	2.40	-1.295
76	0.11	2.839	4.30	-1.044
69	0.08	2.936	6.00	-0.906
66	0.09	2.890	7.60	-0.602
71	0.07	2.982	9.30	-0.558
42	0.06	2.817	*	-0.751

* 25.00 ml of 0.20 M FTA added

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MeTTA - UO_2^{2+} - TBP

Variant - TBP (0.987 M)

pH = 1.19

D_o - undeterminable

d_b	d_a	log (D_s-D_o)	V	log [TBP]
0.15	85	-2.754	1.90	-1.398
0.21	87	-2.618	2.40	-1.295
0.28	86	-2.487	3.20	-1.170
0.45	82	-2.260	4.30	-1.044
0.82	88	-2.031	6.00	-0.906
1.2	84	-1.845	7.60	-0.602
1.8	84	-1.670	9.30	-0.558

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MeTTA - Th^{4+} - TBP   Variant - TBP (0.987 M)

pH = 2.88 D_o = 0.032

d_b	d_a	log (D_s-D_o)	V	log TBP
44	872	-1.737	0.05	-3.006
67	856	-1.336	0.10	-2.699
97	830	-1.072	0.20	-2.391
115	782	-0.940	0.40	2.084
187	714	-0.639	0.70	1.837
200	690	-0.589	1.00	1.679
218	676	-0.537	1.40	1.530
235	642	-0.477	1.90	1.395
276	632	-0.393	2.40	1.292
240	634	-0.460	3.20	1.167
294	620	-0.375	4.30	1.041
294	600	-0.339	6.00	0.902

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TA - UO_2^{2+} - TBP　　Variant - TBP (0.987 M)

pH = 2.48　D_o = 0.0007

d_b	d_a	log (D_s-D_o)	V	log [TBP]
19	65	-0.534	0.05	-3.006
26	38	-0.165	0.10	-2.701
48	30	0.204	0.40	-2.087
71	19	0.573	0.70	-1.836
73	15	0.687	1.00	-1.682
75	11	0.834	1.40	-1.533
78	8.9	0.943	1.90	-1.398
71	7.8	0.961	2.40	-1.295
69	5.6	1.091	3.20	-1.170
71	4.0	1.249	4.30	-1.044
80	3.2	1.398	6.00	-0.906
81	2.2	1.566	7.60	-0.602
74	1.7	1.639	9.70	-0.531

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$TTA - UO_2^{2+} - TBP$ Variant - TBP (0.987 M)

pH = 1.23 $D_o = 0.214$

d_b	d_a	$\log (D_s-D_o)$	V	$\log [TBP]$
69	9.5	0.848	0.05	-3.006
81	8.7	0.959	0.10	-2.701
82	2.9	1.448	0.20	-2.398
90	1.4	1.807	0.40	-2.087
86	1.1	1.892	0.70	-1.836
83	0.73	2.055	1.00	-1.682
86	0.60	2.156	1.40	-1.533
92	0.37	2.395	1.90	-1.398
81	0.41	2.295	2.40	-1.295
81	0.19	2.630	3.20	-1.170
86	0.17	2.704	4.30	-1.044
81	0.25	2.510	6.00	-0.906
80	0.10	2.903	7.60	-0.602
76	0.08	2.978	9.30	-0.558
62	0.14	2.646	*	-0.644
45	0.07	2.821	*	-0.781

* 10.00 ml of 0.20 M TTA added

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AA - UO_2^{2+} Variant - AA (0.792 M)

pH = 3.21

d_b	d_a	log D_o	V	log [AA]
0.07	71	-3.004	0.63	-2.006
0.10	79	-2.897	1.25	-1.710
0.22	77	-2.544	1.88	-1.532
0.38	75	-2.295	2.50	-1.411
0.60	74	-2.091	3.13	-1.314
0.82	76	-1.967	3.75	-1.235
1.5	77	-1.811	4.38	-1.169
2.0	68	-1.532	5.00	-1.113
2.3	78	-1.530	5.64	-1.062
2.8	68	-1.385	6.25	-1.019
4.3	74	-1.236	8.05	-0.914
7.2	65	-0.956	10.00	-0.828
9.5	65	-0.835	13.00	-0.730
1.3	61	-0.671	15.00	-0.678
5.7	67	-1.070	*	-0.852
2.8	69	-1.392	*	-0.931

* 25.00 ml of benzene added

AA - UO_2^{2+} - TBP Variant - AA (0.396 M)

pH = 3.04

d_b	d_a	log D	V	log [AA]
21	70	-0.523	1.50	-1.938
35	51	-0.164	3.00	-1.645
54	33	0.214	4.50	-1.481
58	23	0.402	6.00	-1.361
66	18	0.564	7.50	-1.273
68	14	0.686	9.00	-1.201
71	9.9	0.856	10.60	-1.131
68	7.8	0.940	12.00	-1.091
69	5.9	1.068	15.40	-0.998
66	4.4	1.176	18.40	-0.937
59	3.8	1.191	21.40	-0.887
60	3.2	1.273	24.40	-0.834
57	2.6	1.341	27.40	-0.801

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AA - UO_2^{2+} - $SO_4^{=}$ - TBP Variant - AA (0.400 M)

pH = 2.53

d_b	d_a	log D	V	log [AA]
0.16	85	-2.725	1.50	-1.934
0.63	95	-2.178	3.00	-1.641
1.4	95	-1.831	5.00	-1.432
2.8	84	-1.477	7.00	-1.297
3.5	82	-1.370	9.00	-1.199
3.8	87	-1.360	11.00	-1.124
5.0	81	-1.209	13.00	-1.063
6.2	81	-1.116	15.00	-1.012
7.6	79	-1.017	17.00	-0.968
9.2	79	-0.934	19.00	-0.931
8.9	76	-0.931	21.00	-0.897
10	75	-0.875	23.00	-0.868
12	72	-0.778	27.00	-0.819

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BA - UO_2^{2+} Variant - BA (0.788 M)

pH = 3.39

d_b	d_a	log D_o	V	log [BA]
0.35	73	-2.319	1.25	-1.714
0.84	74	-1.945	1.88	-1.537
1.6	70	-1.641	2.50	-1.414
2.5	70	-1.447	3.13	-1.317
4.8	70	-1.164	3.75	-1.240
6.2	70	-1.053	4.38	-1.173
8.2	66	-0.906	5.00	-1.117
14	63	-0.653	5.63	-1.066
15	58	-0.588	6.25	-1.022
21	55	-0.418	8.03	-0.918
31	42	-0.132	9.65	-0.854
38	32	0.075	11.35	-0.791
44	29	0.181	13.05	-0.738
32	33	-0.013	*	-0.817
22	38	-0.238	*	-0.885

* 10.00 ml of benzene added

BA - UO_2^{2+} - TBP Variant - BA (0.394 M)

pH = 3.26

d_b	d_a	log D	V	log [BA]
0.59	71	-2.080	0.00	
26	47	-0.257	0.63	-2.309
50	34	0.168	1.25	-2.013
61	17	0.555	1.88	-1.837
66	8.8	0.875	2.50	-1.618
63	6.7	0.973	3.13	-1.540
72	4.9	1.167	3.75	-1.474
74	3.6	1.313	4.38	-1.474
74	2.8	1.422	5.02	-1.417
30	1.0	1.477	10.02	-1.140
61	0.74	1.916	15.02	-0.995
54	0.53	2.008	20.02	-0.901

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BTA - UO_2^{2+} Variant - BTA (0.809 M)

pH = 3.22

d_b	d_a	log D_o	V	log [BTA]
19	57	-0.477	0.63	-1.997
37	44	-0.075	1.25	-1.699
53	25	0.325	1.88	-1.520
59	14	0.625	2.50	-1.398
68	8.9	0.883	3.13	-1.302
68	6.4	1.027	3.75	-1.225
72	4.0	1.255	4.38	-1.159
73	3.3	1.345	5.00	-1.103
71	1.9	1.573	6.25	-1.009
75	1.4	1.729	8.03	-0.906
64	1.1	1.765	9.65	-0.832
41	1.3	1.499	*	-0.927

* 30.00 ml of benzene added.

BTA - UO_2^{2+} - TBP Variant - BTA (0.405 M)

pH = 1.22

d_b	d_a	log D	V	log [BTA]
69	1.6	1.635	8.75	-1.191
59	0.93	1.802	10.00	-1.139
70	0.64	2.039	11.25	-1.094
53	0.54	1.992	12.50	-1.054
54	0.31	2.241	15.50	-0.976
52	0.28	2.269	18.50	-0.915
52	0.18	2.461	21.50	-0.866
47	0.19	2.393	24.50	-0.826

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$BTA - UO_2^{2+} - NO_3^-$ Variant - BTA (0.811 M)

pH = 2.95

d_b	d_a	log D_o	V	log [BTA]
21	91	-0.637	0.63	-1.996
35	74	-0.325	1.25	-1.699
49	59	-0.081	1.88	-1.495
65	40	0.211	2.50	-1.379
79	29	0.345	3.13	-1.287
84	21	0.602	3.75	-1.206
78	15	0.716	4.38	-1.149
82	13	0.800	5.00	-1.090
78	9.4	0.919	5.63	-1.045
92	6.9	1.125	6.25	-1.001
89	4.1	1.337	8.00	-0.901
85	3.0	1.452	9.65	-0.827
85	2.1	1.607	11.35	-0.765
80	1.6	1.699	13.05	-0.713

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DBM - UO_2^{2+} Variant - DBM (0.799 M)

pH = 3.37

d_b	d_a	log D_o	V	log [DBM]
0.01	70	-2.854	0.63	-2.003
0.33	74	-2.347	1.25	-1.706
0.82	71	-1.939	1.88	-1.530
1.4	68	-1.686	2.50	-1.405
2.3	64	-1.445	3.13	-1.309
4.3	72	-1.224	3.75	-1.232
6.3	64	-1.007	4.38	-1.166
8.8	64	-0.862	5.00	-1.110
10	62	-0.792	5.63	-1.059
18	54	-0.477	8.05	-0.913
26	55	-0.325	9.65	-0.841
35	40	-0.058	11.35	-0.779
35	32	0.039	13.05	-0.727
25	39	-0.193	*	-0.807
13	46	-0.549	**	-0.960

* 10.00 ml of benzene added

** 25.00 ml of benzene added

DBM - UO_2^{2+} - TBP Variant - DBM (0.399 M)

pH = 3.01

d_b	d_a	log D	V	log [DBM]
31	37	-0.077	0.63	-2.304
50	20	0.398	1.25	-2.007
65	23	0.451	1.88	-1.831
74	12	0.790	2.50	-1.708
70	3.3	1.327	3.13	-1.612
69	3.3	1.320	3.75	-1.534
76	1.2	1.802	4.38	-1.468
83	0.97	1.932	5.00	-1.412
78	0.99	1.897	7.50	-1.244
67	0.53	2.102	15.00	-1.132
66	0.55	2.176	15.00	-0.986
61	0.45	2.132	20.00	-0.891
55	0.41	2.127	25.00	-0.818

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FTA - UO_2^{2+} Variant - FTA (0.836 M)

pH = 3.08

d_b	d_a	log D_o	V	log [FTA]
32	48	-0.176	0.63	-1.983
59	21	0.449	1.25	-1.686
66	12	0.740	1.88	-1.510
73	7.8	0.971	2.50	-1.387
80	3.9	1.312	3.13	-1.291
77	2.5	1.489	3.75	-1.214
84	1.8	1.669	4.38	-1.147
80	0.94	1.930	5.00	-1.091
78	0.77	2.006	5.90	-1.021
78	0.67	2.066	6.40	-0.987
78	0.53	2.168	8.00	-0.894
69	0.57	2.083	9.60	-0.821
82	0.39	2.323	11.20	-0.761
64	0.41	2.193	12.80	-0.711
45	0.33	2.135	*	-0.891
34	0.23	2.170	*	-1.019

* 25.00 ml of benzene added

FTA UO_2^{2+} - TBP Variant - FTA (0.418 M)

pH = 1.19

d_b	d_a	log D	V	log [FTA]
68	22	0.490	1.25	-1.991
69	6.3	1.040	2.50	-1.697
82	2.9	1.451	3.75	-1.527
79	1.7	1.667	5.00	-1.408
80	0.94	1.930	7.00	-1.272
83	0.67	2.093	9.00	-1.175
78	0.47	2.220	11.00	-1.099
70	0.34	2.314	13.00	-1.038
66	0.30	2.342	15.00	-0.987
65	0.20	2.512	18.00	-0.924
62	0.16	2.588	21.00	-0.873
60	0.15	2.602	24.00	-0.813
55	0.09	2.772	27.00	-0.796
53	0.11	2.683	30.00	-0.766
38	0.15	2.404	*	-0.905
29	0.22	2.120	*	-1.012

* 25.00 ml of 0.2 M TBP added

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MeTTA - UO_2^{2+} - TBP Variant - MeTTA (0.173 M)

pH = 3.15

d_b	d_a	log D	V	log [MeTTA]
2.5	72	-1.460	2.00	-2.176
6.9	73	-1.025	6.00	-1.726
16	61	-0.581	11.00	-1.498
24	50	-0.319	15.00	-1.387
28	39	-0.144	20.00	-1.292
31	33	-0.027	24.00	-1.236
33	25	0.121	29.00	-1.180
36	22	0.214	33.00	-1.144
36	20	0.255	38.00	-1.108
32	15	0.329	42.00	-1.087
33	13	0.405	47.00	-1.056

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TA - UO_2^{2+} Variant - TA (0.806 *M*)

pH = 3.44

d_b	d_a	log D_o	V	log [TA]
1.8	78	-1.637	0.63	-1.999
4.8	76	-1.200	1.25	-1.802
9.0	73	-0.909	1.88	-1.526
17	68	-0.602	2.50	-1.403
20	57	-0.455	3.13	-1.307
27	57	-0.324	3.75	-1.229
32	49	-0.185	4.38	-1.163
38	47	-0.092	5.00	-1.091
50	32	0.194	6.25	-1.001
55	27	0.309	8.55	-0.877
61	16	0.581	10.85	-0.787
63	10	0.799	13.15	-0.718

TA - UO_2^{2+} - TBP Variant - TA (0.403 *M*)

pH = 3.32

d_b	d_a	log D	V	log [TA]
32	40	-0.097	0.63	-2.300
50	21	0.377	1.25	-2.003
57	9.6	0.774	1.88	-1.827
69	4.7	1.167	2.50	-1.704
64	3.1	1.315	3.17	-1.608
65	2.4	1.433	3.75	-1.530
62	1.9	1.514	4.38	-1.464
58	1.4	1.617	5.00	-1.408
63	0.64	1.993	10.00	-1.130
59	0.44	2.127	15.00	-0.985
47	0.32	2.167	20.00	-0.880
48	0.31	2.190	25.00	-0.816

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TTA - UO_2^{2+} Variant - TTA (0.796 M)

pH = 3.15

d_b	d_a	log D_o	V	log [TTA]
36	42	-0.067	0.63	-2.004
58	24	0.383	1.25	-1.707
57	8.8	0.811	1.88	-1.531
67	4.8	1.145	2.50	-1.409
74	3.6	1.313	3.13	-1.312
70	2.5	1.447	3.75	-1.235
74	2.3	1.507	4.38	-1.168
73	1.4	1.717	5.00	-1.111
72	1.3	1.743	5.63	-1.061
58	1.0	1.763	6.25	-1.017
66	0.83	1.901	7.95	-0.926

TTA - UO_2^{2+} - TBP Variant - TTA (0.398 M)

pH = 1.22

d_b	d_a	log D	V	log [TTA]
65	2.6	1.398	5.00	-1.430
72	1.2	1.778	6.25	-1.339
72	0.98	1.866	7.50	-1.266
69	0.76	1.958	8.75	-1.205
61	0.52	2.069	10.00	-1.153
58	0.39	2.172	11.25	-1.108
50	0.67	2.169	15.50	-1.068
56	0.21	2.426	18.50	-0.929
61	0.18	2.530	21.50	-0.880
57	0.15	2.580	24.50	-0.793

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AA - UO_2^{2+} Variant - pH

$E^{o\prime}$ = -372.1 mv $HClO_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
13	69	-0.725	0.000	-182.1	3.167
11	72	-0.816	0.005	-186.2	3.100
7.1	76	-1.030	0.015	-195.9	2.937
4.2	78	-1.269	0.025	-204.1	2.800
2.5	76	-1.483	0.050	-213.7	2.640
1.3	80	-1.788	0.080	-224.9	2.453
0.73	80	-2.041	0.110	-232.6	2.325
0.50	81	-2.208	0.150	-241.3	2.180
0.31	82	-2.409	0.190	-246.6	2.090
0.20	80	-2.602	0.240	-253.8	1.972

AA - UO_2^{2+} - TBP Variant - pH

$E^{o\prime}$ = -374.0 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
61	3.9	1.194	0.000	-195.3	2.978
65	4.8	1.132	0.010	-202.0	2.867
60	8.0	0.875	0.030	-216.4	2.627
57	12	0.677	0.050	-225.0	2.483
55	17	0.510	0.070	-231.7	2.372
47	21	0.350	0.100	-239.3	2.245
45	26	0.238	0.140	-245.5	2.142
35	34	0.012	0.200	-253.7	2.005
28	42	-0.176	0.280	-259.7	1.905
19	45	-0.374	0.390	-267.6	1.773
15	55	-0.564	0.520	-274.9	1.652
11	60	-0.737	0.670	-281.7	1.538
8.6	58	-0.829	0.850	-288.3	1.428
6.5	61	-0.972	1.060	-294.1	1.332

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AA - UO_2^{2+} - SO_4^{2-} - TBP Variant - pH

$E^{o\prime}$ = -378.3 mv H_2SO_4 (0.67 M)

d_b	d_a	log D	V	E	pH
29	65	-0.350	0.000	-229.3	2.483
17	77	-0.656	0.030	-236.9	2.357
8.6	88	-1.010	0.070	-249.1	2.153
6.2	86	-1.142	0.110	-255.4	2.048
4.2	92	-1.340	0.160	-261.4	1.947
2.6	100	-1.585	0.230	-268.2	1.835
1.5	89	-1.773	0.310	-274.6	1.728
0.88	95	-2.033	0.400	-280.1	1.637
0.73	98	-2.128	0.520	-286.5	1.530
0.54	100	-2.268	0.650	-292.9	1.423
0.34	99	-2.465	0.800	-298.2	1.335
0.32	90	-2.449	1.020	-304.7	1.227
0.15	98	-2.815	1.300	-311.8	1.108

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BA - UO_2^{2+} Variant - pH

$E^{o'}$ = -375.6 mv $HClO_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
42	39	0.032	0.000	-178.8	3.280
16	61	-0.581	0.005	-198.0	2.960
12	66	-0.740	0.010	-202.0	2.893
7.7	72	-0.971	0.020	-209.9	2.762
3.8	75	-1.295	0.035	-218.1	2.625
2.4	74	-1.489	0.050	-225.0	2.510
1.7	74	-1.638	0.070	-231.9	2.395
0.97	78	-1.842	0.100	-239.3	2.272
0.66	77	-2.067	0.140	-247.7	2.132
0.39	80	-2.313	0.190	-254.4	2.020
0.25	81	-2.510	0.250	-261.6	1.900

BA - UO_2^{2+} - TBP (0.20 M) Variant - pH

$E^{o'}$ = -374.1 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
81	1.5	1.732	0.000	-200.0	2.902
79	2.4	1.518	0.010	-210.0	2.735
71	3.7	1.283	0.020	-219.0	2.585
74	5.8	1.106	0.040	-227.6	2.442
68	9.1	0.870	0.075	-237.0	2.285
66	16	0.615	0.110	-246.8	2.122
60	22	0.436	0.150	-253.3	2.013
50	33	0.180	0.220	-264.4	1.828
41	41	0.000	0.290	-271.4	1.712
34	45	-0.121	0.380	-278.2	1.598
28	52	-0.269	0.490	-284.9	1.487
23	56	-0.386	0.620	-291.0	1.385
18	68	-0.577	0.785	-297.7	1.273
13	71	-0.737	1.000	-304.0	1.168

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BA - UO_2^{2+} - TBP (0.10 M) Variant - pH

$E^{o'}$ = -376.1 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
66	0.78	1.928	0.000	-197.8	2.972
65	1.0	1.813	0.010	-206.2	2.832
62	2.2	1.450	0.030	-218.6	2.625
64	3.6	1.250	0.050	-226.4	2.495
64	6.6	0.987	0.080	-235.5	2.343
57	11	0.715	0.120	-243.2	2.215
53	17	0.494	0.170	-250.8	2.089
50	24	0.319	0.230	-257.7	1.973
43	36	0.077	0.300	-264.0	1.868
36	49	-0.134	0.390	-270.8	1.755
26	55	-0.325	0.510	-277.9	1.637
19	63	-0.520	0.660	-285.0	1.518
13	73	-0.749	0.850	-291.8	1.405
9.0	76	-0.927	1.090	-298.6	1.292

BA - UO_2^{2+} - TBP (0.05 M) Variant - pH

$E^{o'}$ = -377.3 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
80	4.0	1.301	0.000	-202.7	2.910
72	6.2	1.065	0.010	-209.8	2.792
74	9.5	0.982	0.025	-218.2	2.652
67	15	0.665	0.050	-226.2	2.518
60	24	0.407	0.080	-234.9	2.373
50	34	0.168	0.120	-243.9	2.223
39	43	-0.037	0.170	-251.4	2.098
27	52	-0.280	0.230	-258.2	1.985
20	49	-0.389	0.300	-265.3	1.867
11	63	-0.780	0.380	-271.8	1.758
10	69	-0.836	0.480	-278.0	1.655
7.5	72	-0.979	0.610	-283.9	1.557
5.8	76	-1.117	0.770	-290.2	1.452
3.8	71	-1.276	0.970	-296.8	1.342

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BA - UO_2^{2+} - TBP (0.01 M) Variant - pH

$E^{o\prime}$ = -368.3 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
68	7.7	0.946	0.000	-194.2	2.902
58	13	0.650	0.010	-203.8	2.742
51	20	0.407	0.030	-210.9	2.623
45	35	0.109	0.050	-221.7	2.443
36	45	-0.097	0.075	-227.3	2.350
25	54	-0.334	0.110	-236.1	2.203
13	61	-0.672	0.160	-246.0	2.038
7.9	67	-0.928	0.210	-254.4	1.898
5.5	75	-1.135	0.280	-262.7	1.760
3.3	75	-1.356	0.370	-270.5	1.630
2.1	73	-1.541	0.470	-277.2	1.518
1.5	77	-1.710	0.610	-283.8	1.408
1.0	78	-1.893	0.780	-290.8	1.292
0.72	87	-2.082	0.980	-297.2	1.185

BA - UO_2^{2+} - TBP (0.002 M) Variant - pH

$E^{o\prime}$ = -375.4 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
49	25	-0.292	0.000	-194.8	3.010
32	44	-0.138	0.020	-208.7	2.728
23	51	-0.346	0.040	-215.5	2.665
13	59	-0.638	0.060	-226.0	2.483
8.3	66	-0.901	0.080	-232.8	2.377
5.7	66	-1.064	0.110	-239.8	2.260
3.4	70	-1.314	0.150	-247.5	2.132
2.0	67	-1.525	0.200	-255.2	2.003
1.2	71	-1.772	0.270	-262.9	1.875
0.78	72	-1.965	0.350	-269.5	1.765
0.48	75	-2.194	0.450	-276.4	1.650
0.27	77	-2.455	0.580	-283.2	1.537
0.25	79	-2.500	0.730	-290.0	1.423
0.15	74	-2.692	0.900	-296.0	1.323

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BA - UO_2^{2+} - Cl^- Variant - pH

$E^{o\prime}$ = -462.0 HCl (1.0 M)

d_b	d_a	log D_o	V	E	pH
46	40	0.061	0.000	-244.0	3.633
29	54	-0.270	0.010	-255.7	3.438
16	65	-0.609	0.030	-264.9	3.285
8.1	74	-0.960	0.045	-275.0	3.117
3.8	76	-1.301	0.060	-285.3	2.945
3.1	76	-1.389	0.085	-289.0	2.883
1.7	78	-1.661	0.100	-296.6	2.757
1.2	88	-1.866	0.120	-302.0	2.667
0.76	87	-2.058	0.150	-309.5	2.542
0.36	86	-2.378	0.195	-317.8	2.403

BA - UO_2^{2+} - Cl^- - TBP Variant - pH

$E^{o\prime}$ = -459.2 HCl (1.0 M)

d_b	d_a	log D	V	E	pH
84	3.2	0.000	1.419	-284.0	2.920
75	5.0	0.020	1.176	-291.8	2.790
75	7.0	0.050	1.030	-299.2	2.667
73	9.1	0.090	0.904	-306.2	2.550
67	15	0.145	0.650	-314.0	2.420
63	20	0.498	0.220	-321.2	2.300
56	31	0.257	0.320	-329.6	2.160
50	40	0.097	0.450	-337.2	2.033
42	44	-0.020	0.600	-344.7	1.908
35	50	-0.155	0.780	-351.4	1.797
29	56	-0.286	0.990	-358.3	1.682
22	62	-0.450	1.230	-363.8	1.590
19	66	-0.541	1.495	-368.6	1.510
16	71	-0.647	1.790	-373.2	1.433

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BA - UO_2^{2+} - SO_4^{2-} - TBP   Variant - pH

$E^{o'}$ = -385.3 mv H_2SO_4 (0.67 M)

d_b	d_a	log D	V	E	pH
20	65	0.512	0.000	-224.6	2.675
31	62	0.301	0.020	-231.6	2.562
31	65	0.322	0.050	-239.7	2.427
30	60	0.301	0.070	-243.2	2.368
29	65	0.350	0.110	-250.0	2.255
26	69	0.424	0.160	-258.2	2.118
24	65	0.433	0.220	-264.2	2.018
21	69	0.517	0.300	-270.8	1.908
15	69	0.663	0.410	-278.3	1.783
6.0	79	1.120	0.550	-284.6	1.695
6.8	83	1.087	0.710	-291.5	1.563
4.1	78	1.279	0.890	-297.0	1.472
2.7	82	1.483	1.110	-302.2	1.385
1.6	83	1.714	1.360	-310.7	1.243

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BTA - UO_2^{2+} Variant - pH

$E^{o'}$ = -373.0 mv HClO$_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
13	80	-0.788	0.000	-269.9	1.732
10	73	-0.863	0.100	-275.1	1.632
7.2	76	-1.024	0.240	-280.3	1.545
5.0	75	-1.176	0.440	-287.2	1.430
3.8	75	-1.295	0.690	-293.6	1.323
2.7	72	-1.426	1.000	-299.8	1.220
2.0	72	-1.556	1.350	-304.2	1.147
1.5	72	-1.682	1.800	-309.8	1.053
1.0	71	-1.851	2.355	-315.2	0.963
0.72	74	-2.012	3.050	-319.8	0.887
0.57	74	-2.113	4.000	-324.9	0.802
0.36	69	-2.282	5.450	-330.8	0.703

BTA - UO_2^{2+} Variant - pH

$E^{o'}$ = -375.1 mv HClO$_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
70	6.4	1.039	0.000	-191.1	3.067
65	8.8	0.865	0.010	-203.6	2.858
67	10	0.823	0.020	-209.1	2.767
65	15	0.637	0.040	-218.8	2.605
61	21	0.474	0.070	-230.8	2.405
52	28	0.269	0.100	-239.3	2.263
45	35	0.109	0.135	-246.3	2.147
38	42	-0.043	0.180	-253.0	2.035
34	49	-0.154	0.230	-259.8	1.922
32	54	-0.230	0.290	-266.0	1.817
25	59	-0.373	0.370	-272.1	1.717
27	59	-0.336	0.490	-275.7	1.657
34	57	-0.231	0.700	-286.0	1.485

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BTA - UO_2^{2+} - NO_3^- Variant - pH

$E^{o\prime}$ = -456.7 mv HNO_3 (2.0 M)

d_b	d_a	log D_o	V	E	pH
180	17	1.025	0.000	-293.3	2.723
170	30	0.753	0.010	-300.0	2.612
160	43	0.571	0.030	-307.0	2.495
110	88	0.097	0.070	-322.0	2.245
78	120	-0.187	0.110	-328.0	2.145
57	140	-0.390	0.170	-334.1	2.043
39	160	-0.613	0.250	-342.0	1.912
25	170	-0.832	0.350	-349.8	1.782
17	170	-1.000	0.470	-356.1	1.677
12	180	-1.176	0.610	-362.1	1.577
8.4	180	-1.331	0.820	-370.3	1.440

BTA - UO_2^{2+} - TBP Variant - pH

$E^{o\prime}$ = -373.1 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
81	0.11	2.867	0.490	-282.8	1.505
91	0.14	2.813	0.750	-290.2	1.382
80	0.22	2.561	1.100	-297.3	1.263
83	0.30	2.442	1.500	-303.8	1.155
84	0.45	2.271	2.010	-310.6	1.042
80	0.72	2.046	2.750	-317.2	0.932
86	1.1	1.893	3.660	-323.0	0.835
89	1.7	1.719	4.900	-329.2	0.732
82	2.6	1.499	6.810	-335.1	0.633
80	5.2	1.187	9.900	-340.9	0.537

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DBM - UO_2^{2+} Variant - pH

$E^{o'}$ = -377.5 mv HClO$_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
32	37	-0.063	0.000	-183.0	3.242
16	44	-0.439	0.010	-189.7	3.130
6.8	67	-0.996	0.030	-207.2	2.838
3.0	66	-1.342	0.050	-218.0	2.658
1.6	70	-1.640	0.070	-226.0	2.525
0.85	68	-1.903	0.090	-233.4	2.402
0.57	60	-2.022	0.120	-240.0	2.292

DBM - UO_2^{2+} - TBP Variant - pH

$E^{o'}$ = -378.5 mv HClO$_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
81	1.2	1.829	0.000	-210.3	2.803
82	1.8	1.659	0.010	-218.5	2.667
81	2.4	1.528	0.025	-225.2	2.555
80	3.3	1.385	0.040	-231.1	2.457
74	6.7	1.043	0.110	-246.7	2.337
68	11	0.791	0.170	-255.9	2.043
71	16	0.647	0.250	-264.2	1.905
60	19	0.499	0.350	-272.7	1.763
56	27	0.317	0.460	-279.2	1.655
56	32	0.243	0.595	-285.8	1.545
45	40	0.051	0.750	-291.9	1.443
39	47	-0.081	0.920	-297.0	1.358
32	51	-0.202	1.155	-303.0	1.258

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FTA - UO_2^{2+} Variant - pH

$E^{o'}$ = -378.2 mv HClO$_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
85	1.3	1.815	0.000	-199.2	2.983
82	1.9	1.635	0.010	-211.0	2.787
84	2.5	1.526	0.030	-218.1	2.668
83	4.1	1.306	0.060	-230.8	2.457
77	9.8	0.866	0.130	-246.0	2.203
72	16	0.653	0.180	-253.1	2.085
64	26	0.391	0.250	-261.0	1.953
58	34	0.232	0.320	-267.1	1.852
47	42	0.049	0.410	-273.7	1.742
43	47	-0.039	0.510	-278.8	1.657
32	49	-0.185	0.650	-284.8	1.557
23	53	-0.362	0.850	-293.1	1.418
19	65	-0.534	1.050	-298.3	1.332

FTA - UO_2^{2+} - TBP Variant - pH

$E^{o'}$ = -376.7 mv HClO$_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
85	0.12	2.850	0.590	-296.1	1.343
88	0.10	2.953	0.890	-302.0	1.245
85	0.17	2.699	1.300	-307.9	1.147
85	0.23	2.568	1.850	-313.4	1.055
84	0.33	2.406	2.550	-319.8	0.948
82	0.50	2.215	3.450	-324.9	0.863
91	0.81	2.050	4.810	-331.8	0.748
88	1.4	1.798	6.510	-337.7	0.650
86	2.3	1.573	6.710	-342.0	0.578

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MeTTA - UO_2^{2+} - TBP　　　Variant - pH

$E^{o\prime}$ = -376.1 mv　　　$HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
69	25	0.424	0.00	-205.6	2.842
66	28	0.372	0.01	-208.0	2.802
53	46	0.062	0.03	-217.6	2.642
39	56	-0.157	0.05	-224.6	2.525
29	70	-0.383	0.08	-234.7	2.357
21	73	-0.541	0.11	-241.0	2.252
13	79	-0.782	0.15	-247.8	2.138
8.6	84	-0.991	0.20	-254.9	2.020
5.4	85	-1.197	0.26	-261.9	1.903
3.2	89	-1.444	0.33	-267.8	1.805
2.2	91	-1.618	0.42	-274.1	1.700
1.4	87	-1.793	0.54	-280.8	1.588
0.95	89	-1.971	0.68	-287.2	1.482

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TA - UO_2^{2+} Variant - pH

$E^{o\prime}$ = -367.8 mv $HClO_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
38	43	-0.053	0.000	-195.7	2.868
15	67	-0.650	0.015	-205.2	2.710
5.2	72	-1.143	0.040	-220.0	2.463
3.3	75	-1.356	0.055	-225.8	2.367
2.1	76	-1.559	0.075	-232.9	2.248
1.4	77	-1.740	0.095	-238.4	2.157
0.92	73	-1.900	0.130	-245.7	2.035
0.61	69	-2.119	0.165	-251.0	1.947
0.32	72	-2.398	0.235	-259.7	1.802
0.19	76	-2.620	0.320	-268.1	1.662

TA - UO_2^{2+} - TBP Variant - pH

$E^{o\prime}$ = -369.1 mv $HClO_4$ (1.994 M)

d_b	d_a	log D	V	E	pH
83	1.1	1.878	0.000	-204.7	2.740
81	2.6	1.494	0.020	-220.0	2.485
79	9.3	0.929	0.110	-247.8	2.105
72	14	0.711	0.150	-249.5	1.993
64	21	0.484	0.200	-256.7	1.873
51	28	0.260	0.280	-264.5	1.743
49	37	0.122	0.370	-271.2	1.632
43	43	0.000	0.470	-277.0	1.535
33	53	-0.205	0.620	-284.2	1.415
26	59	-0.356	0.820	-291.9	1.287
20	61	-0.484	1.040	-298.0	1.185
17	65	-0.582	1.300	-303.5	1.093
10	70	-0.845	1.700	-310.2	0.982

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TTA - UO_2^{2+} Variant - pH

$E^{o\prime}$ = -378.2 mv $HClO_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
74	0.64	2.063	0.000	-207.3	2.848
52	0.64	1.910	0.010	-216.2	2.700
73	0.95	1.886	0.025	-221.8	2.607
75	2.6	1.460	0.050	-230.7	2.458
54	4.5	1.079	0.110	-245.0	2.220
65	14	0.667	0.165	-253.9	2.072
57	20	0.455	0.245	-262.0	1.937
34	32	0.027	0.350	-271.3	1.782
39	42	-0.032	0.460	-278.5	1.662
27	30	-0.046	0.600	-285.0	1.553
22	57	-0.413	0.785	-292.0	1.437
14	64	-0.660	1.230	-303.9	1.238
8.6	56	-0.814	1.580	-310.5	1.128

TTA - UO_2^{2+} - TBP Variant - pH

$E^{o\prime}$ = -376.5 mv $HClO_4$ (1.994 M)

d_b	d_a	log D_o	V	E	pH
83	0.14	2.773	0.720	-302.9	1.227
82	0.23	2.552	1.100	-308.0	1.142
81	0.25	2.511	1.600	-313.7	1.047
73	0.47	2.191	2.300	-319.8	0.945
86	0.78	2.042	3.300	-326.0	0.842
83	1.2	1.840	4.800	-332.8	0.728
82	1.9	1.635	6.800	-339.2	0.622
82	3.5	1.370	9.800	-345.4	0.518
74	7.0	1.024	14.800	-354.4	0.368

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TTA - UO_2^{2+} - Cl^- Variant - pH

$E^{o\prime}$ = -462.0 mv HCl (2.0 M)

d_b	d_a	log D_o	V	E	pH
88	3.3	1.426	0.000	-293.4	2.813
90	5.0	1.255	0.010	-299.9	2.702
86	8.2	1.021	0.025	-306.0	2.600
80	15	0.727	0.055	-316.1	2.432
68	29	0.370	0.100	-327.0	2.250
55	40	0.138	0.150	-334.8	2.120
40	55	-0.138	0.220	-344.0	1.967
27	66	-0.388	0.300	-352.0	1.833
19	77	-0.608	0.400	-358.8	1.720
12	85	-0.850	0.550	-367.8	1.570

TTA - UO_2^{2+} - Cl^- - TBP Variant - pH

$E^{o\prime}$ = -461.2 mv HCl (2.0 M)

d_b	d_a	log D	V	E	pH
90	0.10	2.954	0.130	-366.8	1.573
90	0.15	2.778	0.280	-372.0	1.487
91	0.25	2.561	0.485	-377.7	1.392
92	0.41	2.351	0.780	-385.0	1.270
89	0.64	2.143	1.180	-392.0	1.153
97	0.98	1.996	1.700	-399.2	1.033
90	1.8	1.699	2.300	-404.8	0.940
91	2.9	1.497	3.100	-410.4	0.847
91	4.3	1.326	4.200	-417.5	0.728
85	6.7	1.104	5.500	-423.0	0.637
79	11	0.862	7.100	-430.4	0.513

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TTA - UO_2^{2+} - SO_4^{2-} - TBP   Variant - pH

$E^{o\prime}$ = -389.9 mv H_2SO_4 (0.67 M)

d_b	d_a	log D	V	E	pH
0.07	94	3.128	0.000	-244.2	2.428
0.16	93	2.764	0.060	-253.6	2.272
0.11	100	2.959	0.140	-263.4	2.108
0.12	105	2.942	0.230	-271.5	1.973
0.17	100	2.770	0.330	-279.0	1.848
0.22	89	2.607	0.450	-286.0	1.732
0.34	91	2.428	0.590	-292.3	1.627
0.45	105	2.368	0.780	-299.2	1.512
0.63	92	2.164	1.030	-306.1	1.397
0.91	93	2.009	1.390	-314.5	1.257
1.3	84	1.810	1.800	-321.3	1.143
2.0	86	1.634	2.250	-327.8	1.035
2.7	100	1.569	2.830	-334.3	0.927
3.7	90	1.386	3.540	-343.2	0.778

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AA - UO_2^{2+} - TBP   Variant - Time (minutes)

d_b	d_a	log D	pH	Time
110	5.2	1.325	3.03	10
110	6.0	1.263	3.03	20
120	5.8	1.315	3.03	30
120	5.3	1.355	3.03	40
80	44	0.259	1.78	10
82	36	0.358	1.85	20
96	36	0.426	1.86	30
85	24	0.549	1.84	50
4.7	97	-1.314	1.06	10
6.8	89	-1.117	1.06	20
8.4	80	-0.979	1.06	50

First set of data is extraction step; succeeding sets are stripping steps.

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BTA - UO_2^{2+} Variant - Time (minutes)

d_b	d_a	log D_o	pH	Time
46	0.87	1.723	2.98	40
45	0.70	1.808	3.08	80
46	1.2	1.584	2.96	120
48	1.1	1.640	2.96	160
23	23	0.000	2.02	10
43	5.9	0.863	2.02	20
47	1.5	1.496	2.02	30
38	1.4	1.434	1.81	10
32	17	1.539	1.81	50
38	8.7	1.611	1.81	90
43	8.0	1.666	1.81	130
44	6.1	0.275	1.16	40
45	1.3	0.640	1.16	80
49	1.2	0.730	1.16	120
51	1.1	0.858	1.16	160

First set of data is extraction step; succeeding set is stripping step.

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BTA - UO_2^{2+} - NO_3^- Variant - Time (minutes)

d_b	d_a	log D_o	pH	Time
89	20	0.648	2.59	40
96	17	0.752	2.57	80
93	20	0.668	2.58	120
95	19	0.699	2.60	160
98	23	0.629	2.63	200
8.0	108	-1.130	1.62	10
7.4	103	-1.440	1.67	20
6.4	101	-1.198	1.65	30
7.2	102	-1.151	1.65	40
7.1	104	-1.166	1.64	80
6.8	99	-1.173	1.66	120
6.4	103	-1.207	1.68	160

First set of data is extraction step; succeeding sets are stripping steps.

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FTA - UO_2^{2+} Variant - Time (minutes)

d_b	d_a	log D	pH	Time
56	0.30	2.271	2.91	40
50	0.50	2.072	2.91	80
55	0.38	2.160	2.91	120
53	0.48	2.043	2.91	160
46	11	0.621	1.93	40
50	8.2	0.785	1.93	70
49	0.91	1.723	1.93	110
38	0.30	2.103	1.93	150
22	33	-0.176	1.13	10
31	25	0.093	1.13	20
39	21	0.269	1.13	30
40	19	0.323	1.13	40
47	12	0.593	1.13	70
56	10	0.748	1.13	110
52	7.0	0.871	1.13	150

First set of data is extraction step, succeeding sets are stripping steps.

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BTA - UO_2^{2+} - TBP Variant - Time (minutes)

d_b	d_a	log D	pH	Time
81	0.03	3.431	1.58	40
77	0.05	3.188	1.58	80
81	0.04	3.306	1.58	120
83	0.06	3.141	1.58	160
83	0.40	2.317	0.98	10
78	0.36	2.336	0.98	20
100	0.40	2.398	0.98	30
80	0.36	2.347	0.98	80
82	0.38	2.334	0.98	120
86	0.34	2.403	0.98	160
82	1.7	1.683	0.66	40
79	1.9	1.619	0.66	80
84	1.8	1.669	0.66	120
77	1.7	1.656	0.66	160

First set of data is extraction step; succeeding sets are stripping steps.

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Figure I

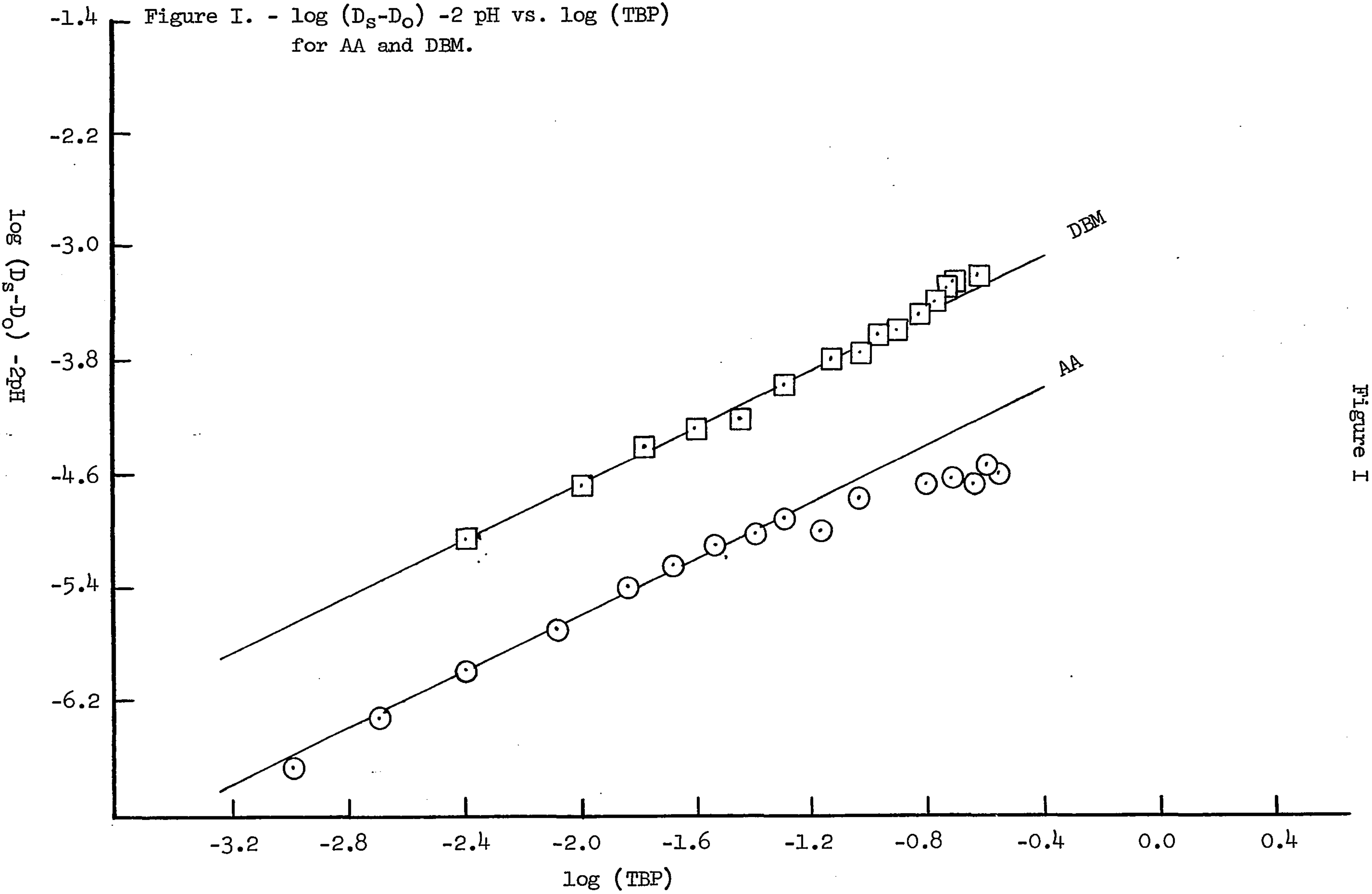

Figure I. - log (D_s-D_o) -2 pH vs. log (TBP) for AA and DBM.

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Figure II

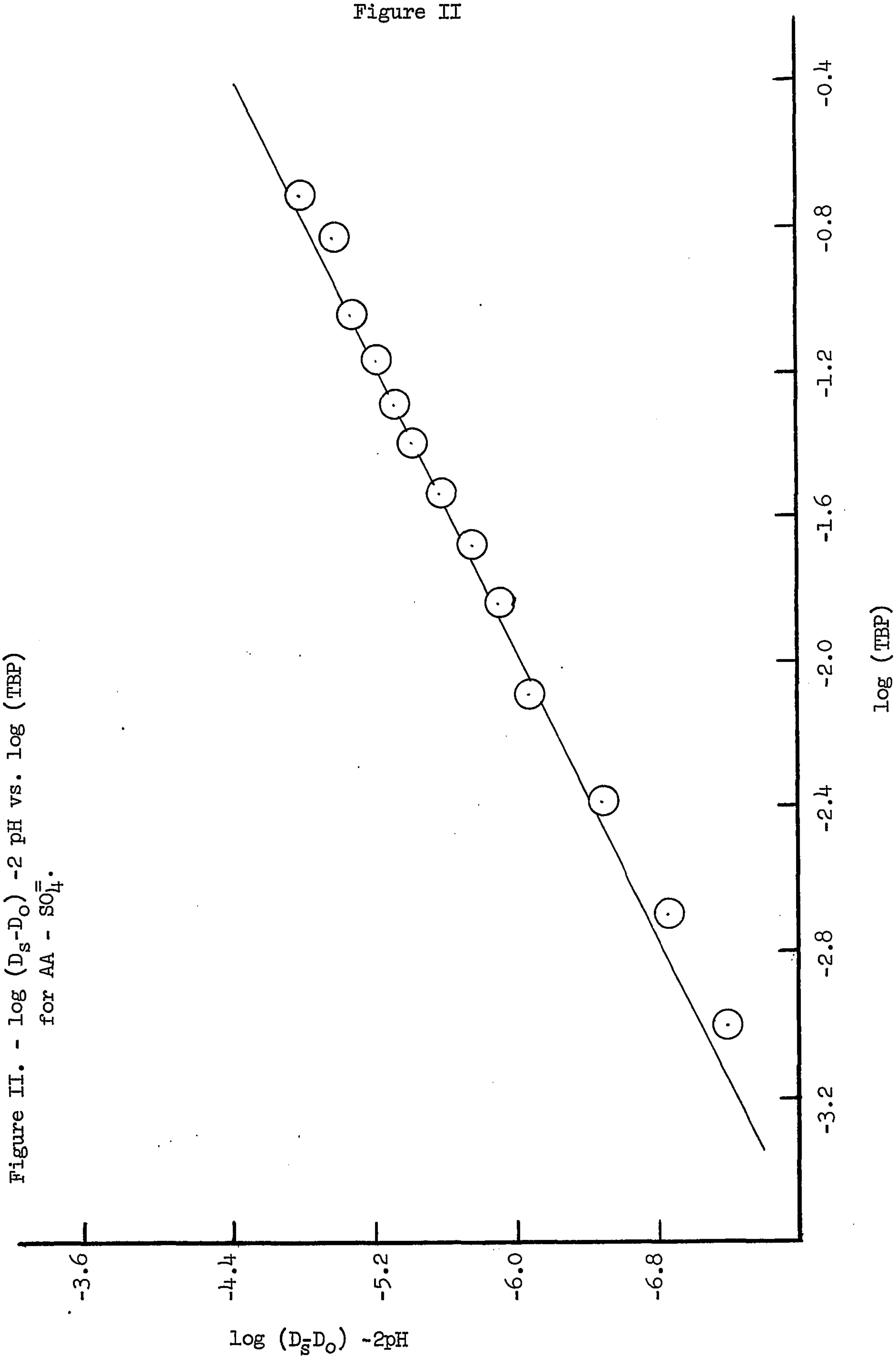

Figure II. - log (D_s-D_o) -2 pH vs. log (TBP) for AA - $SO_4^=$.

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Figure III

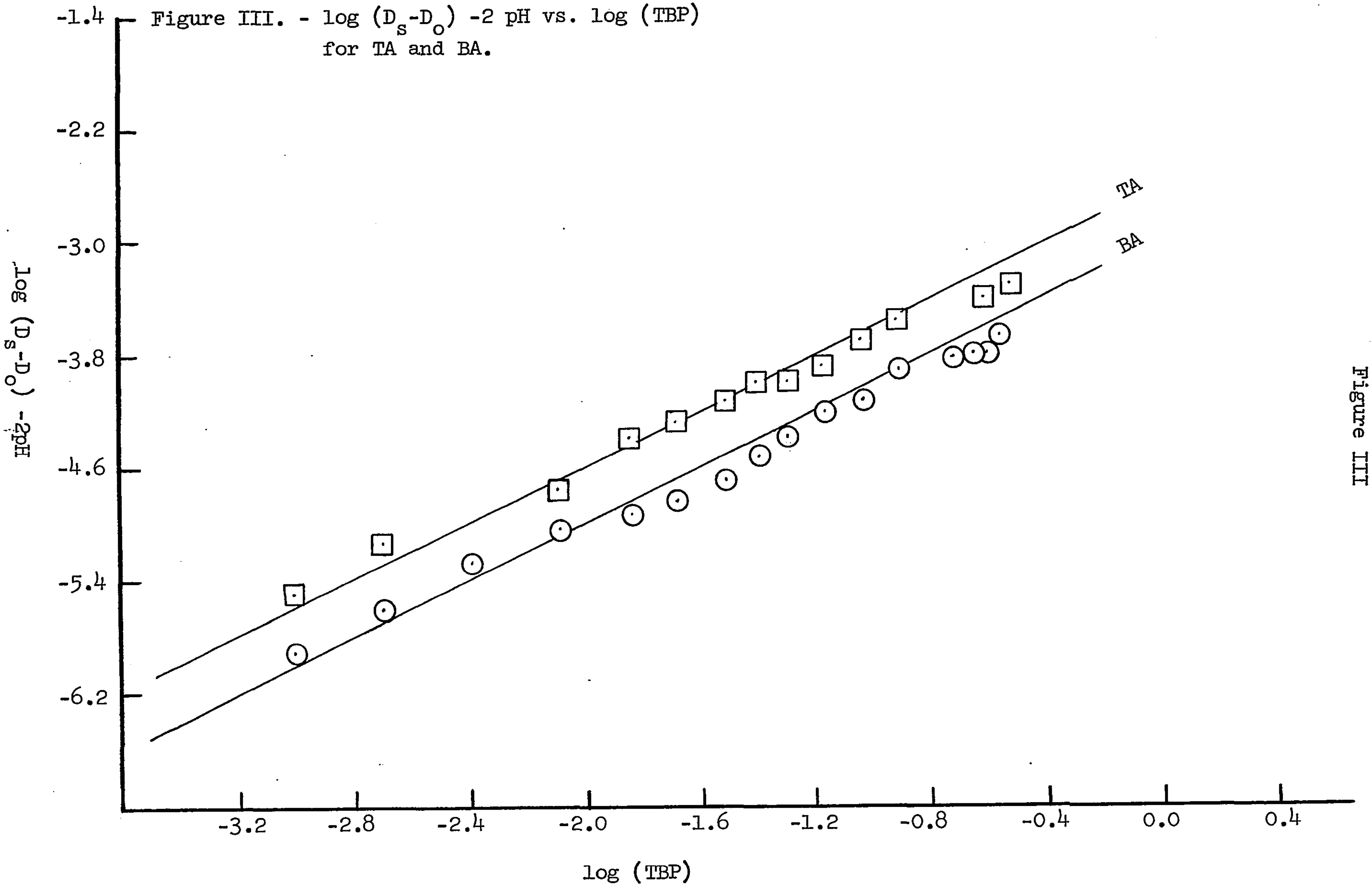

Figure III. - $\log (D_s - D_o) - 2$ pH vs. log (TBP) for TA and BA.

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Figure IV

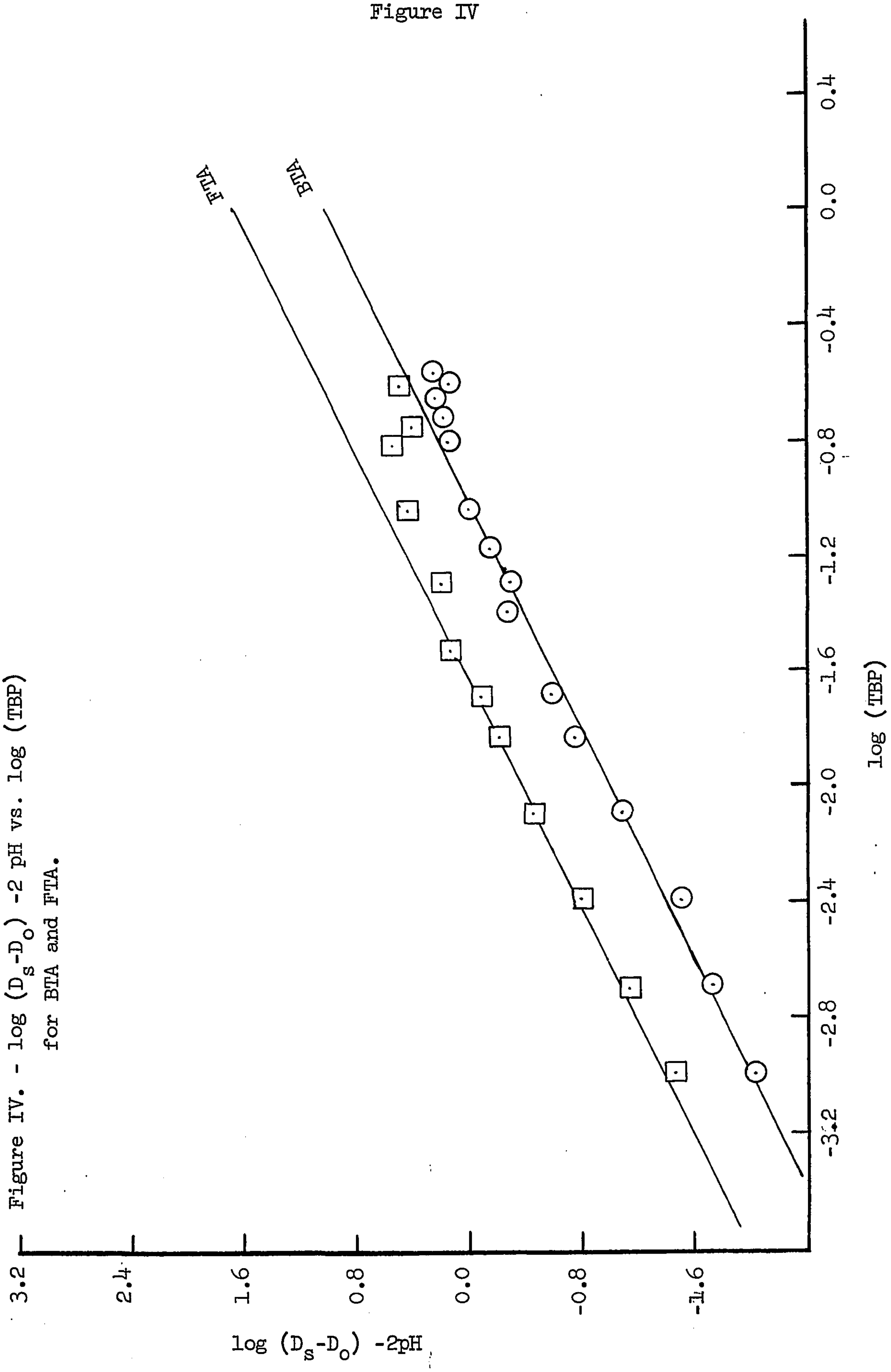

Figure IV. - log (D_s-D_o) -2 pH vs. log (TBP) for BTA and FTA.

Figure V

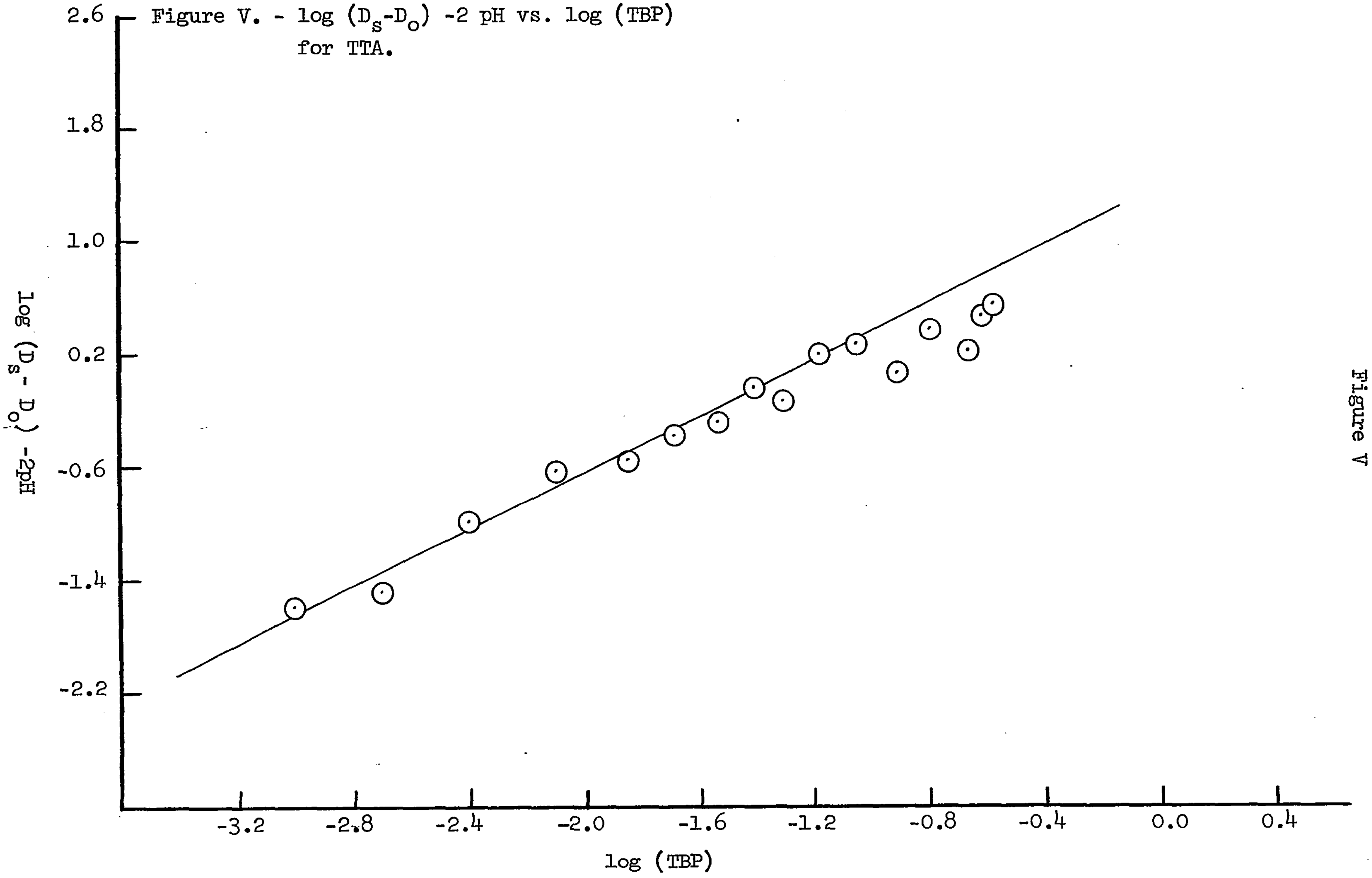

Figure V. - log $(D_s\text{-}D_o)$ -2 pH vs. log (TBP) for TTA.

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Figure VI

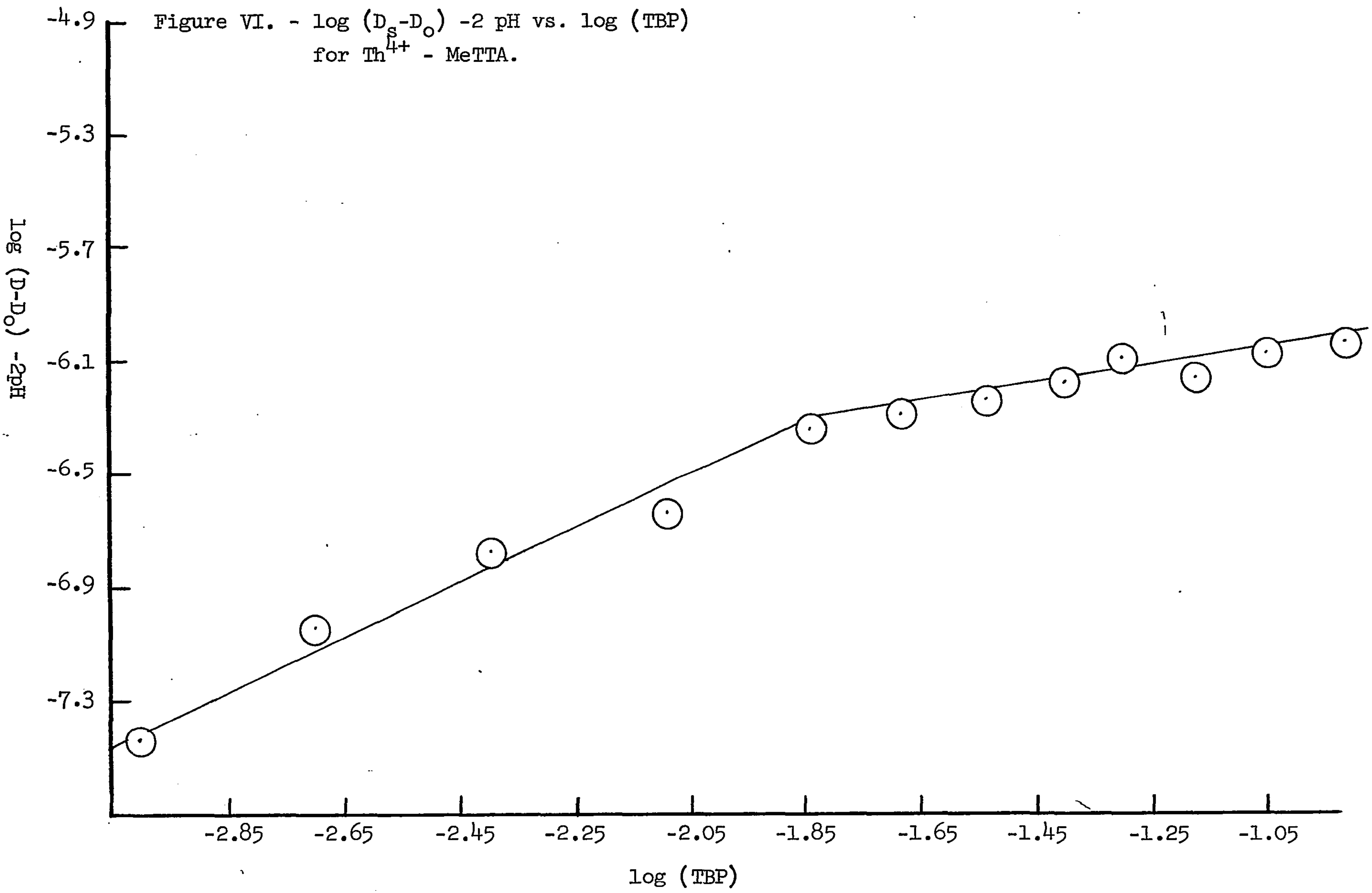

Figure VI. - log (D_s-D_o) -2 pH vs. log (TBP) for Th^{4+} - MeTTA.

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Figure VII

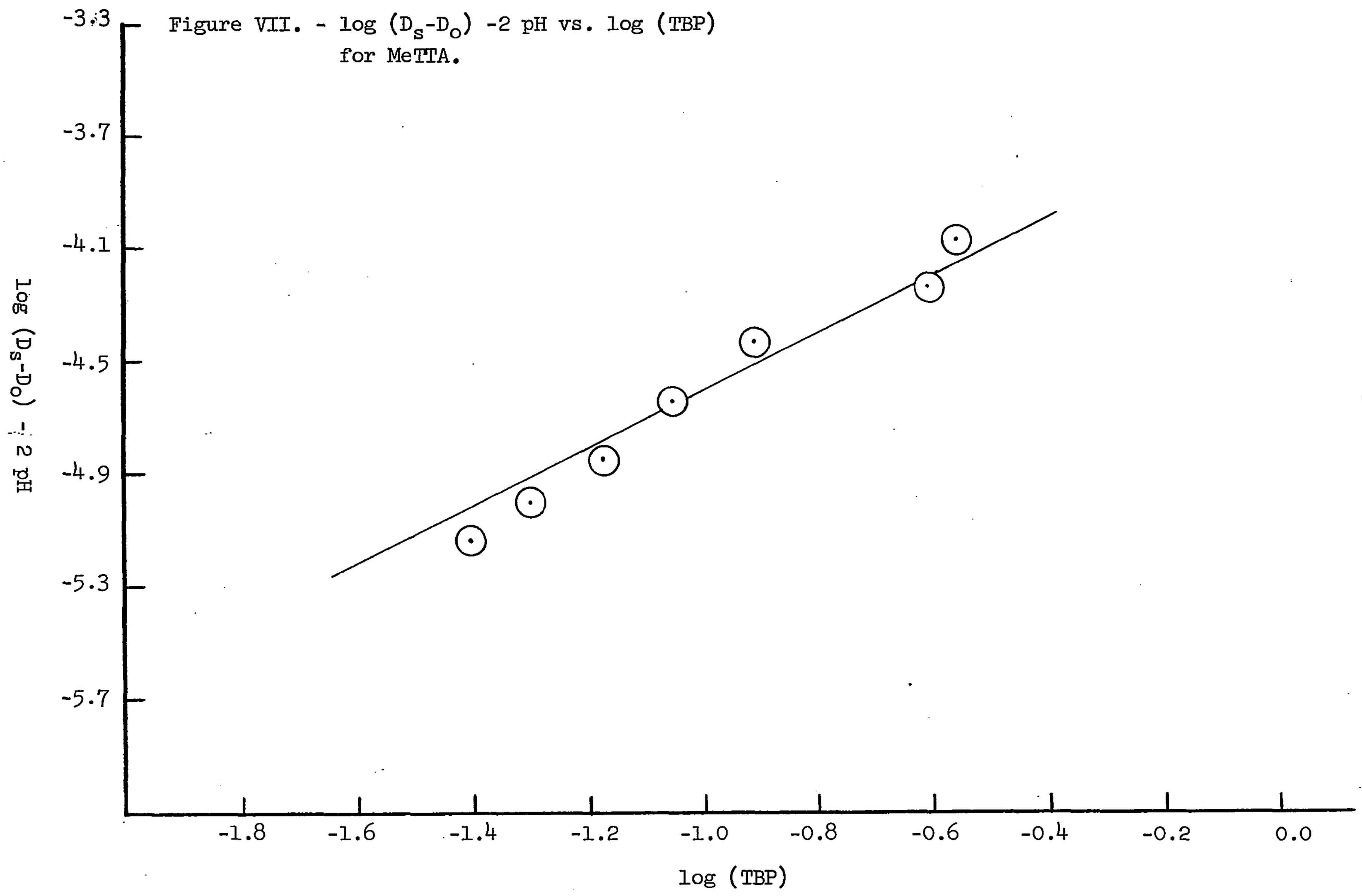

Figure VII. - log (D_s-D_o) -2 pH vs. log (TBP) for MeTTA.

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Figure VIII

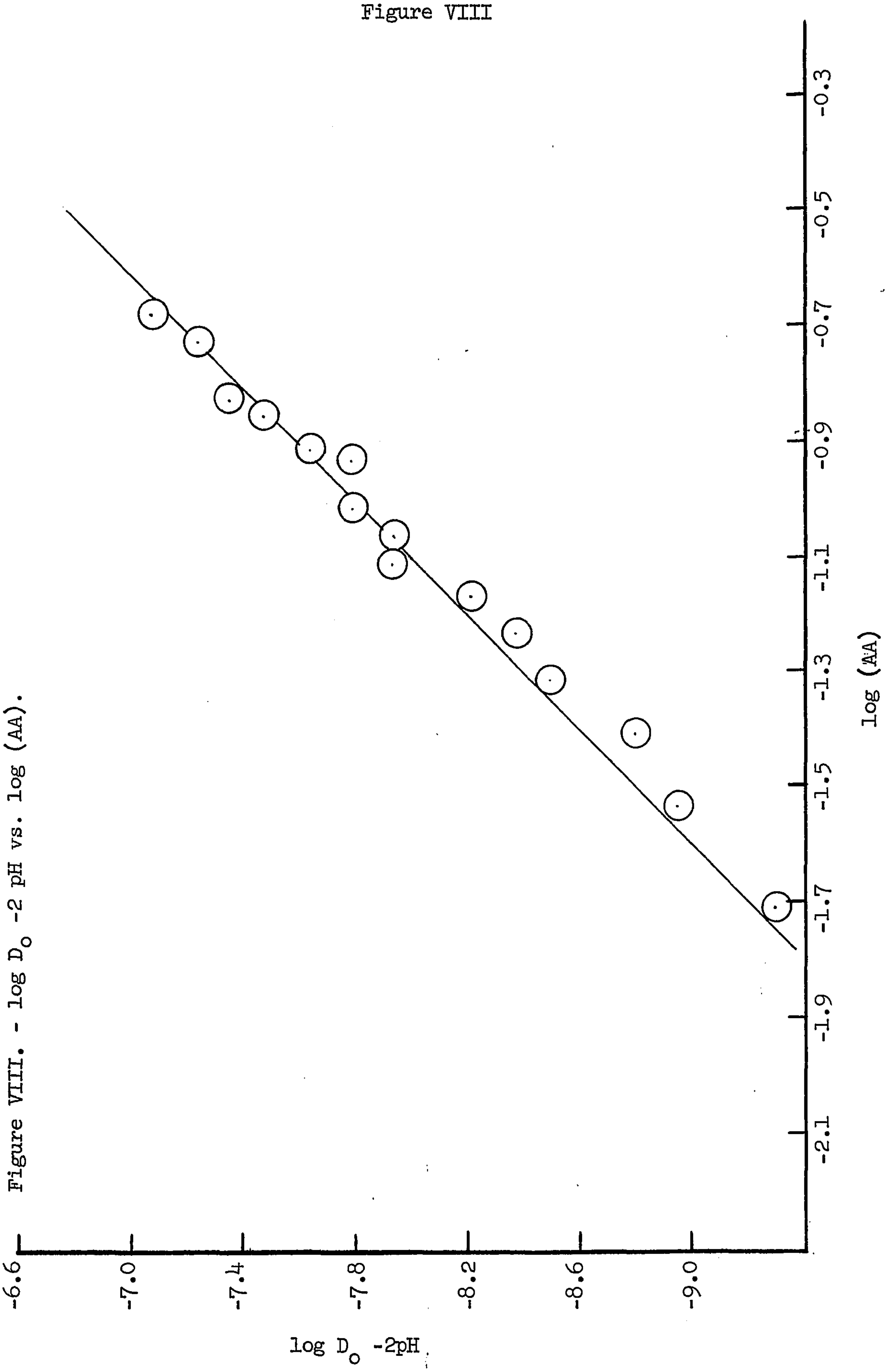

Figure VIII. - log D_o -2 pH vs. log (AA).

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Figure IX

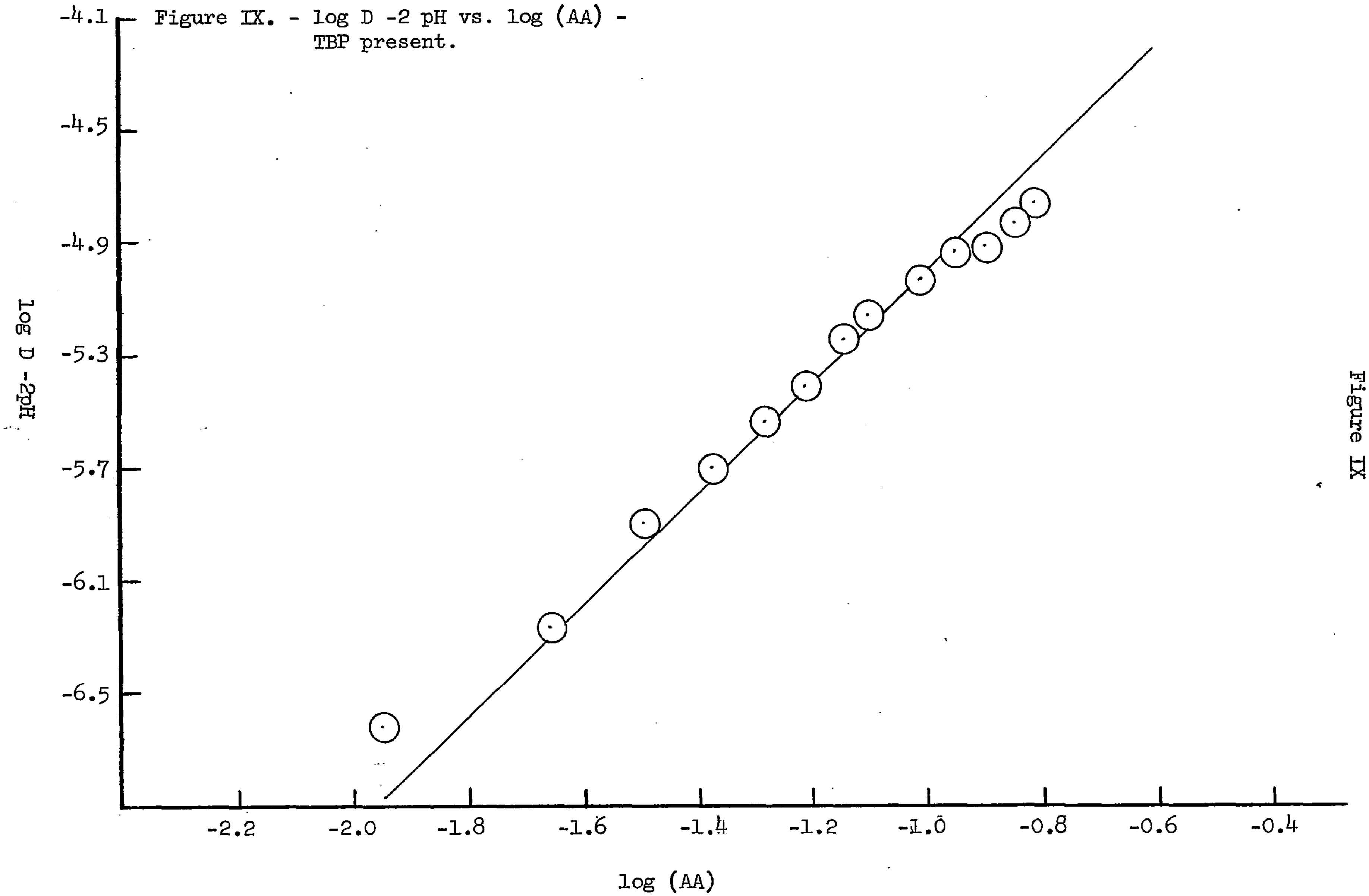

Figure IX. - log D -2 pH vs. log (AA) - TBP present.

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Figure X

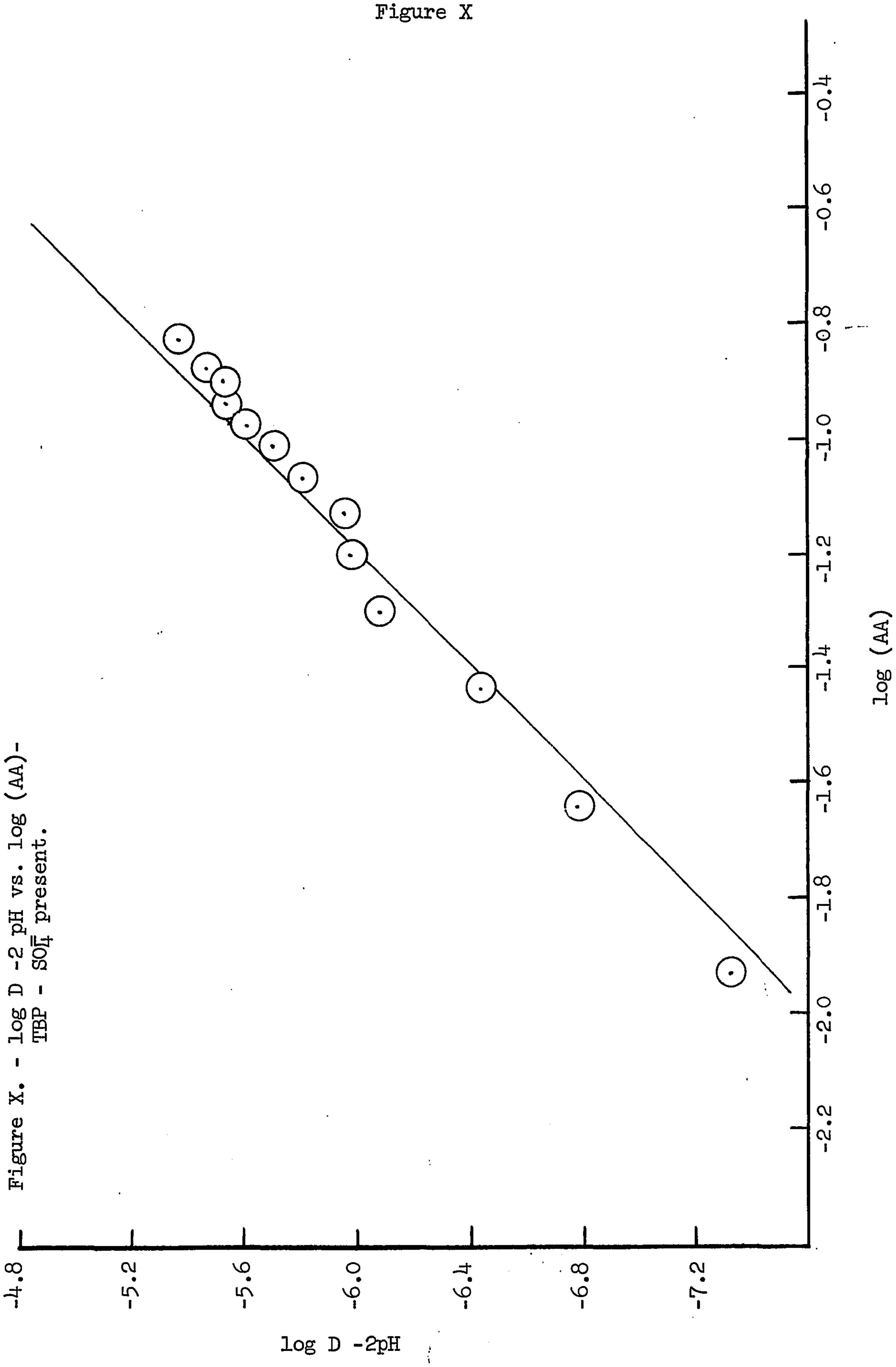

Figure X. - log D -2 pH vs. log (AA)-
TBP - $SO_4^=$ present.

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Figure XI

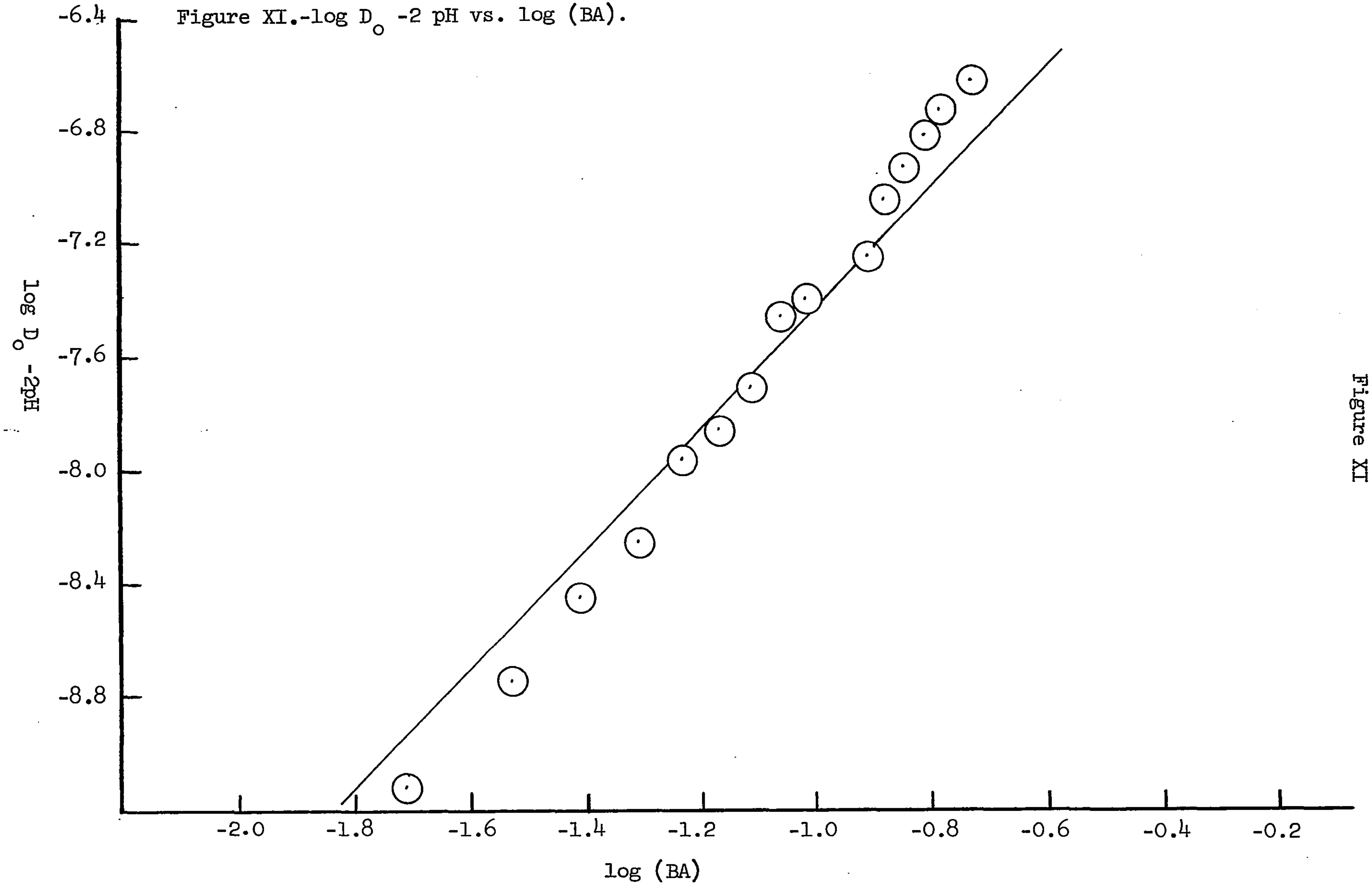

Figure XI.-log D_o -2 pH vs. log (BA).

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Figure: XII

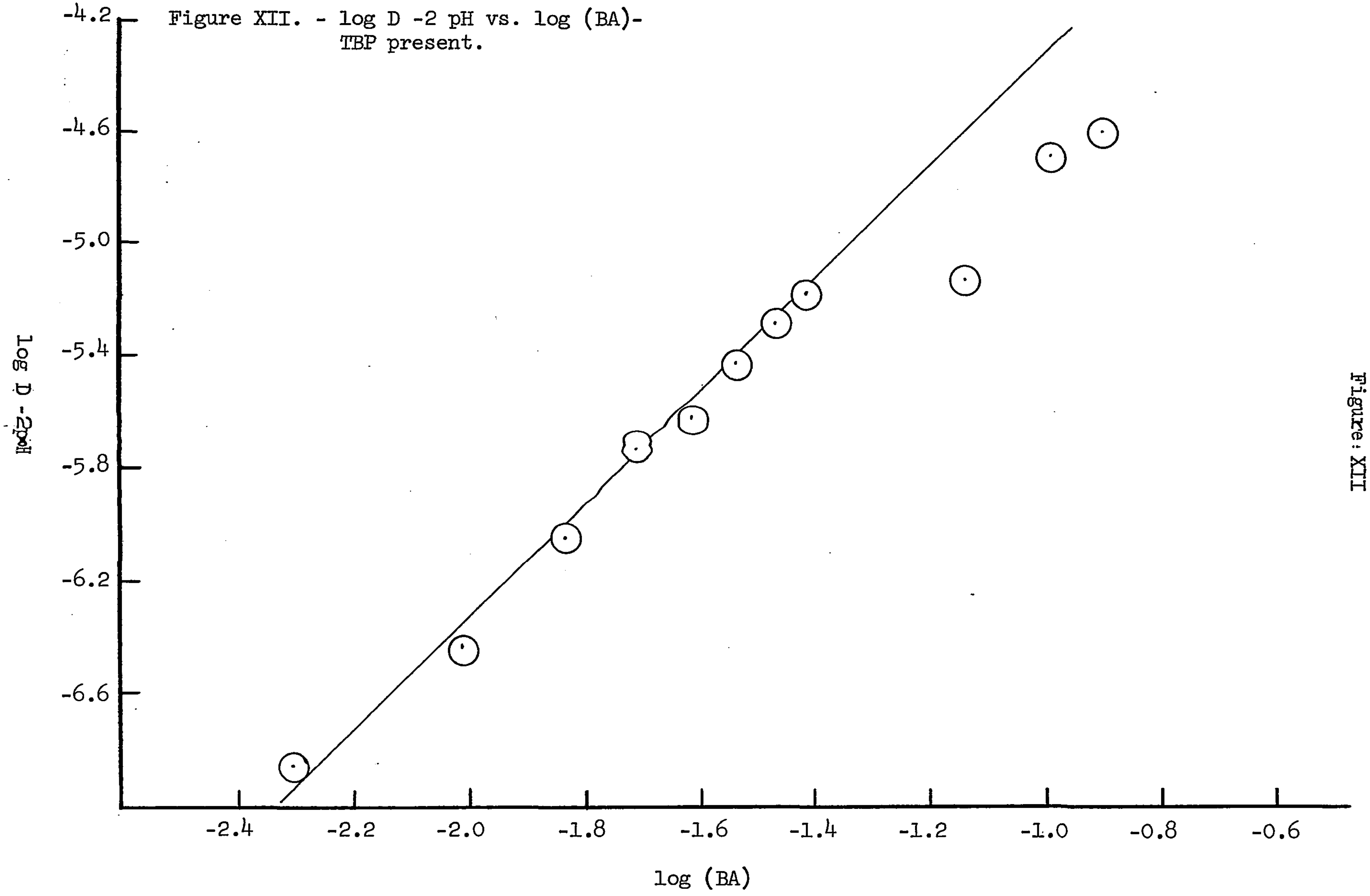

Figure XII. - log D -2 pH vs. log (BA)-
TBP present.

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Figure XIII

Figure XIII. - log D_o -2 pH vs. log (BTA).

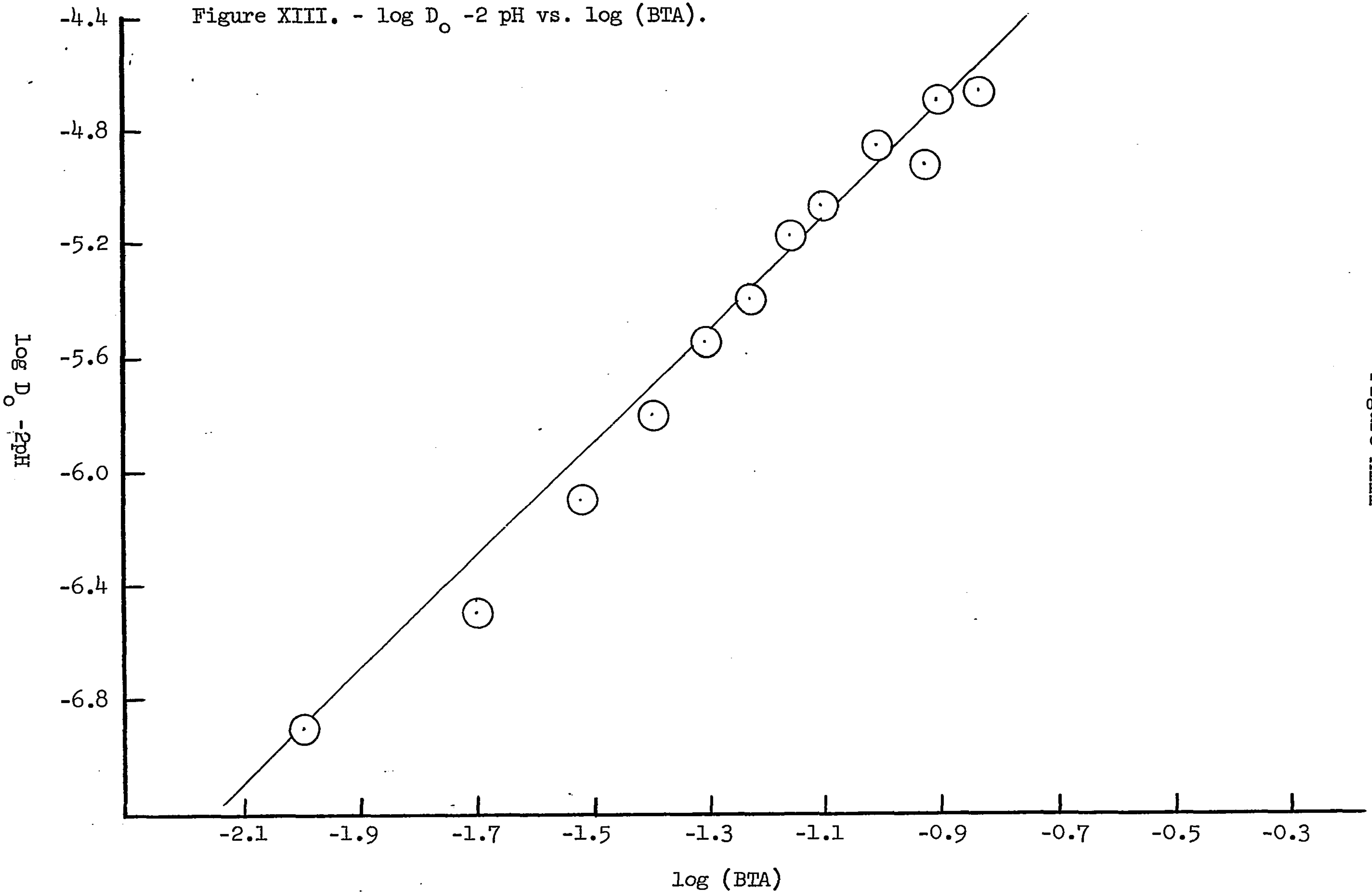

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Figure XIV

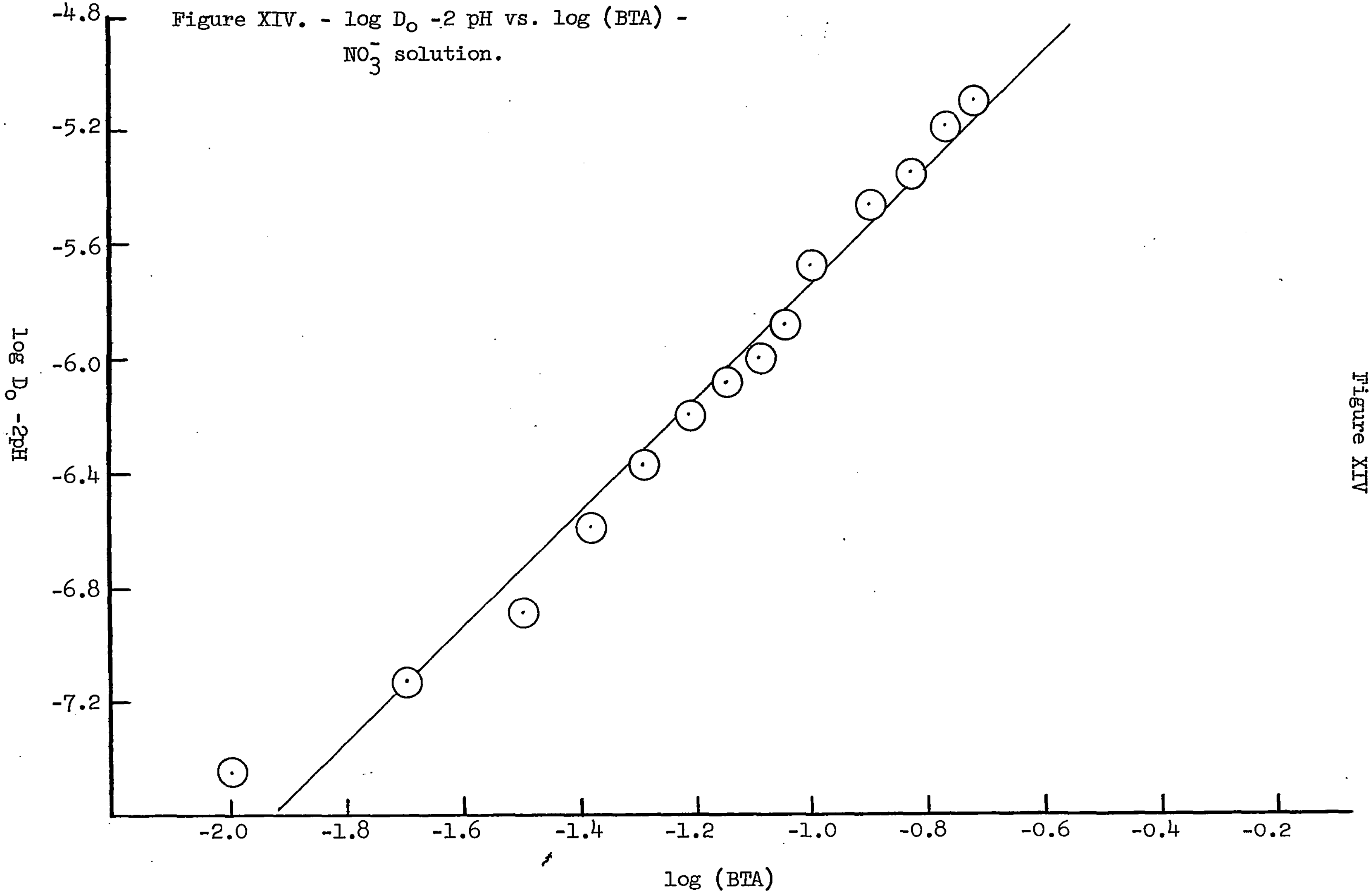

Figure XIV. - log D_o -2 pH vs. log (BTA) - NO_3^- solution.

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Figure XV

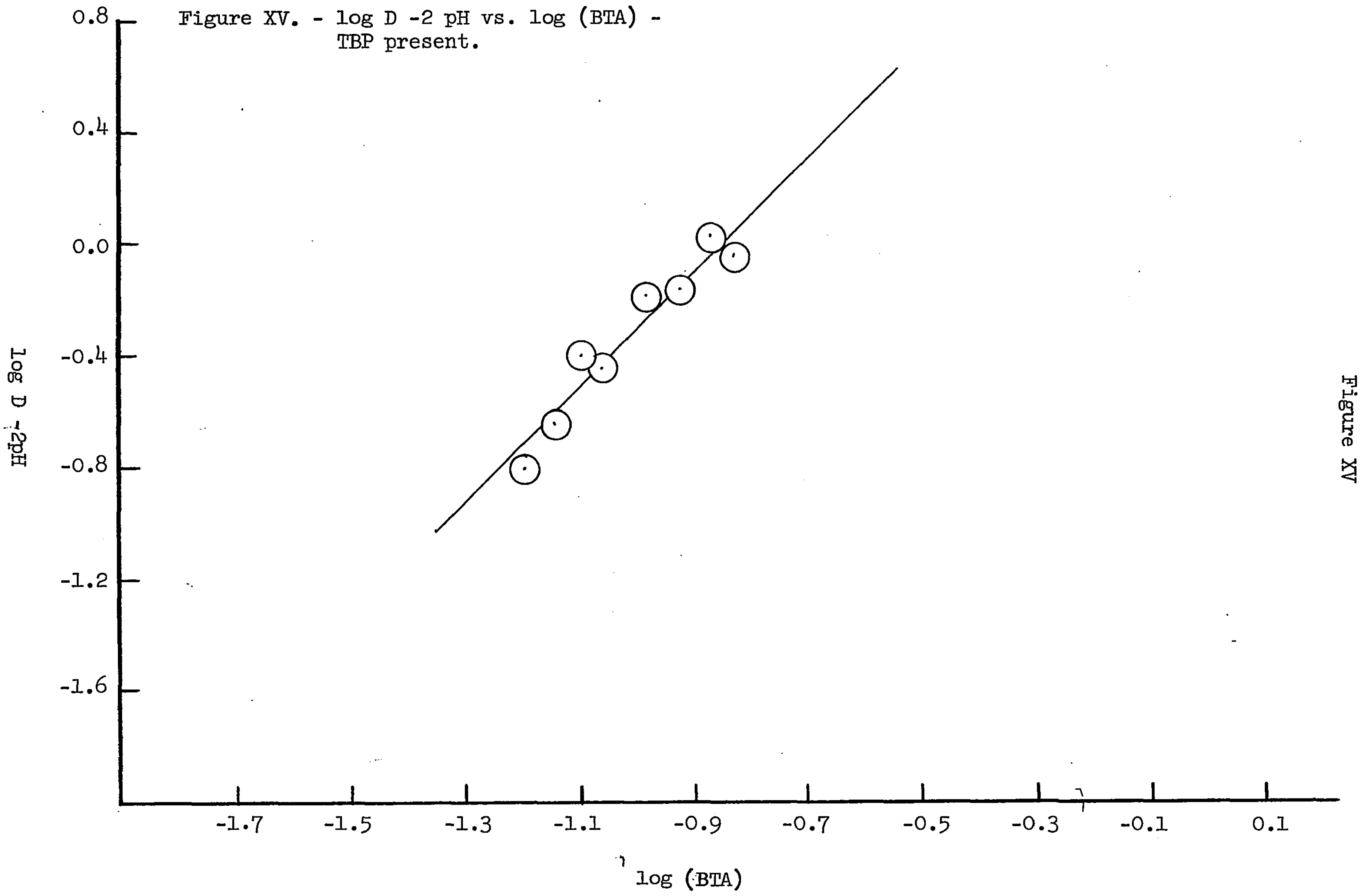

Figure XV. - log D -2 pH vs. log (BTA) -
TBP present.

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Figure XVI

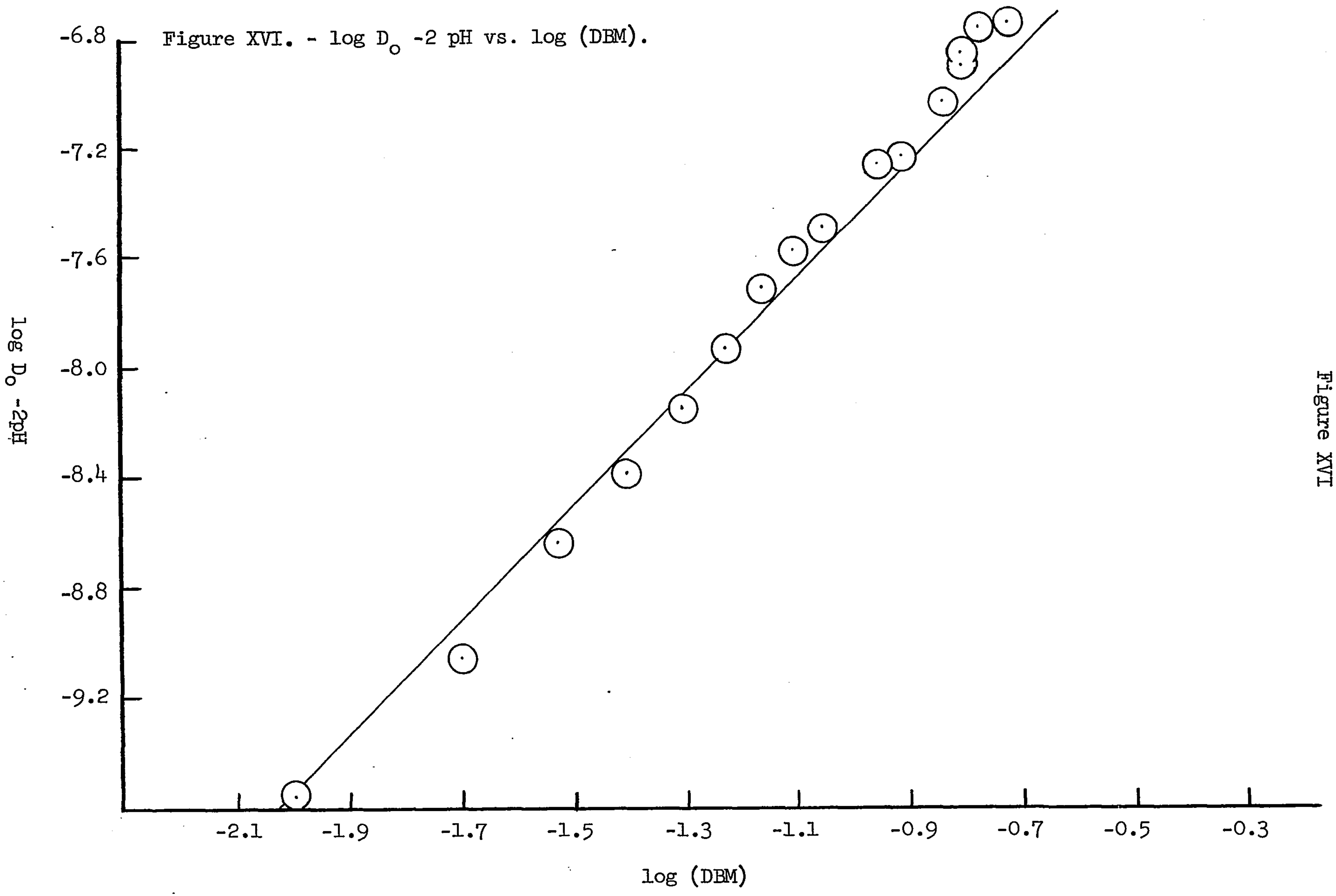

Figure XVI. - log D_o -2 pH vs. log (DBM).

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Figure XVII

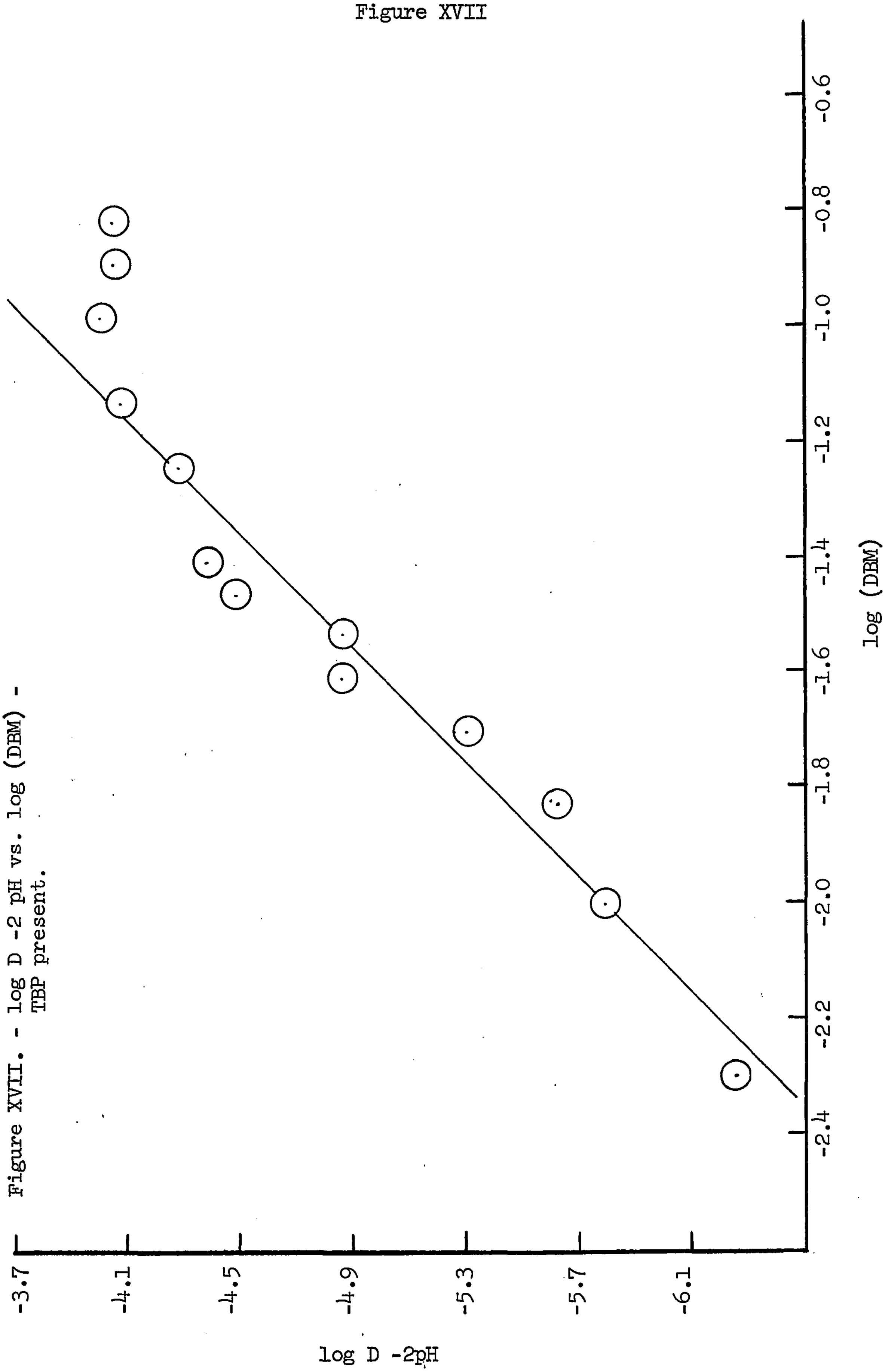

Figure XVII. - log D -2 pH vs. log (DBM) - TBP present.

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Figure XVIII

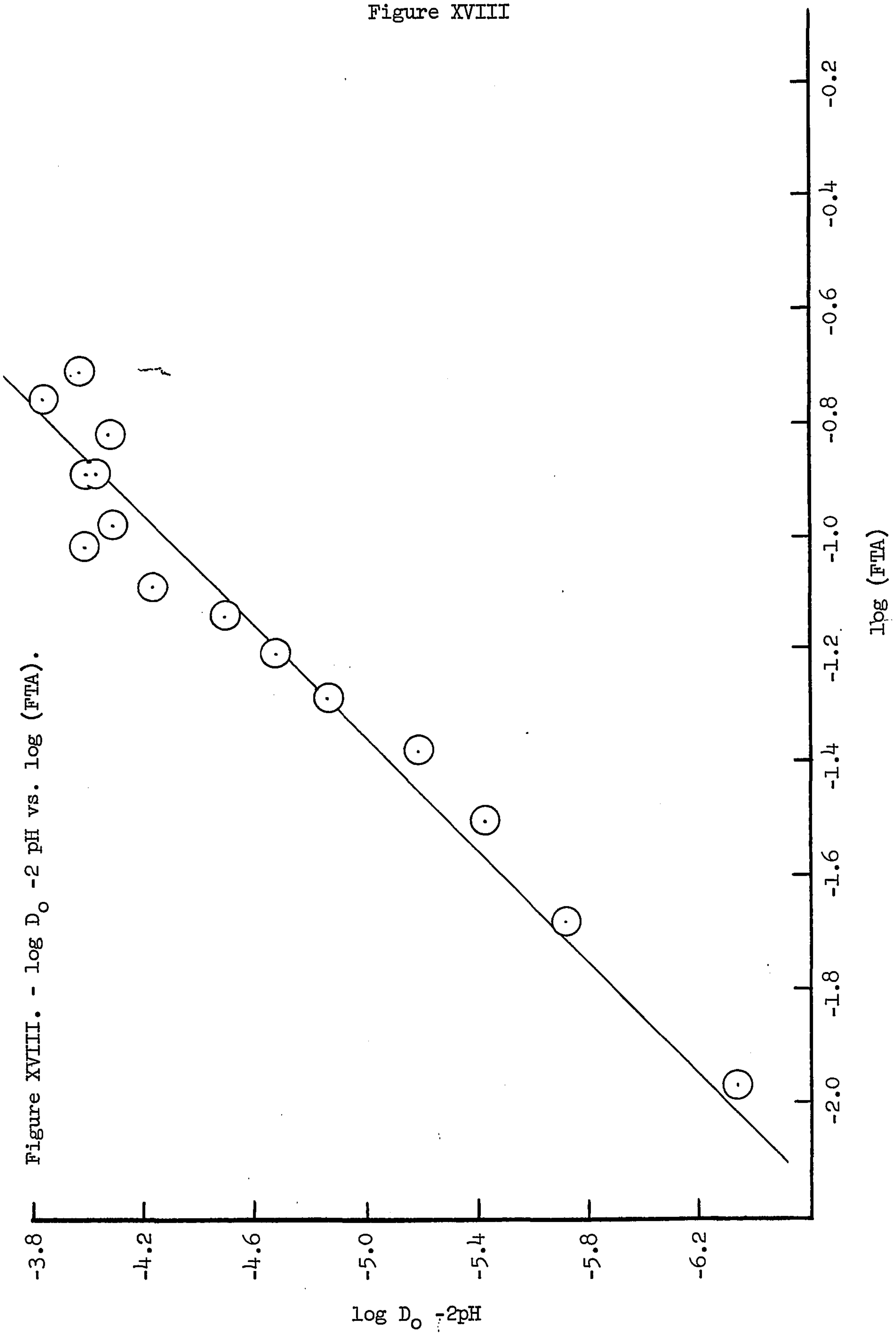

Figure XVIII. - $\log D_o$ -2 pH vs. log (FTA).

Figure XIX

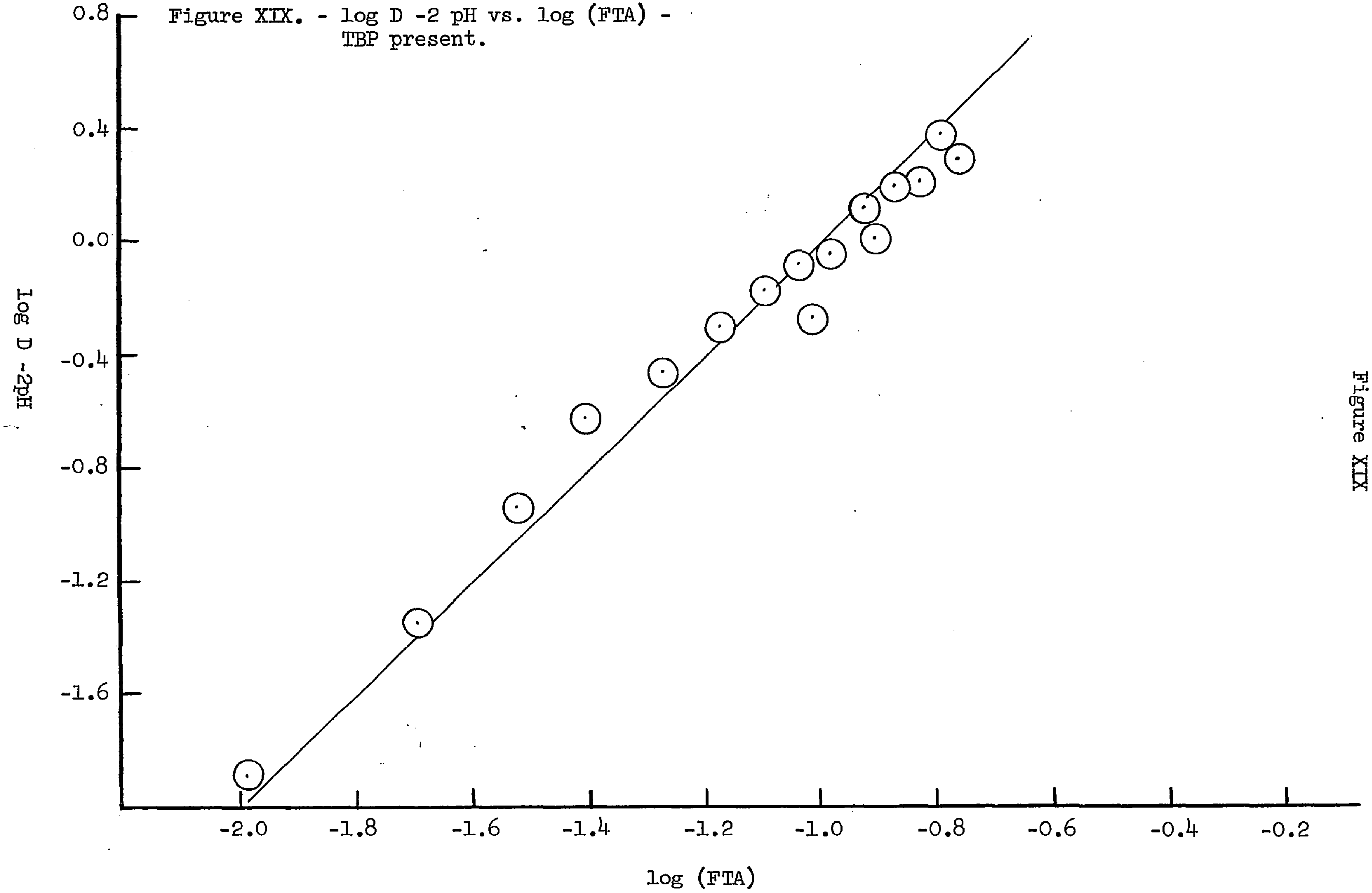

Figure XIX. - log D -2 pH vs. log (FTA) - TBP present.

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Figure XX

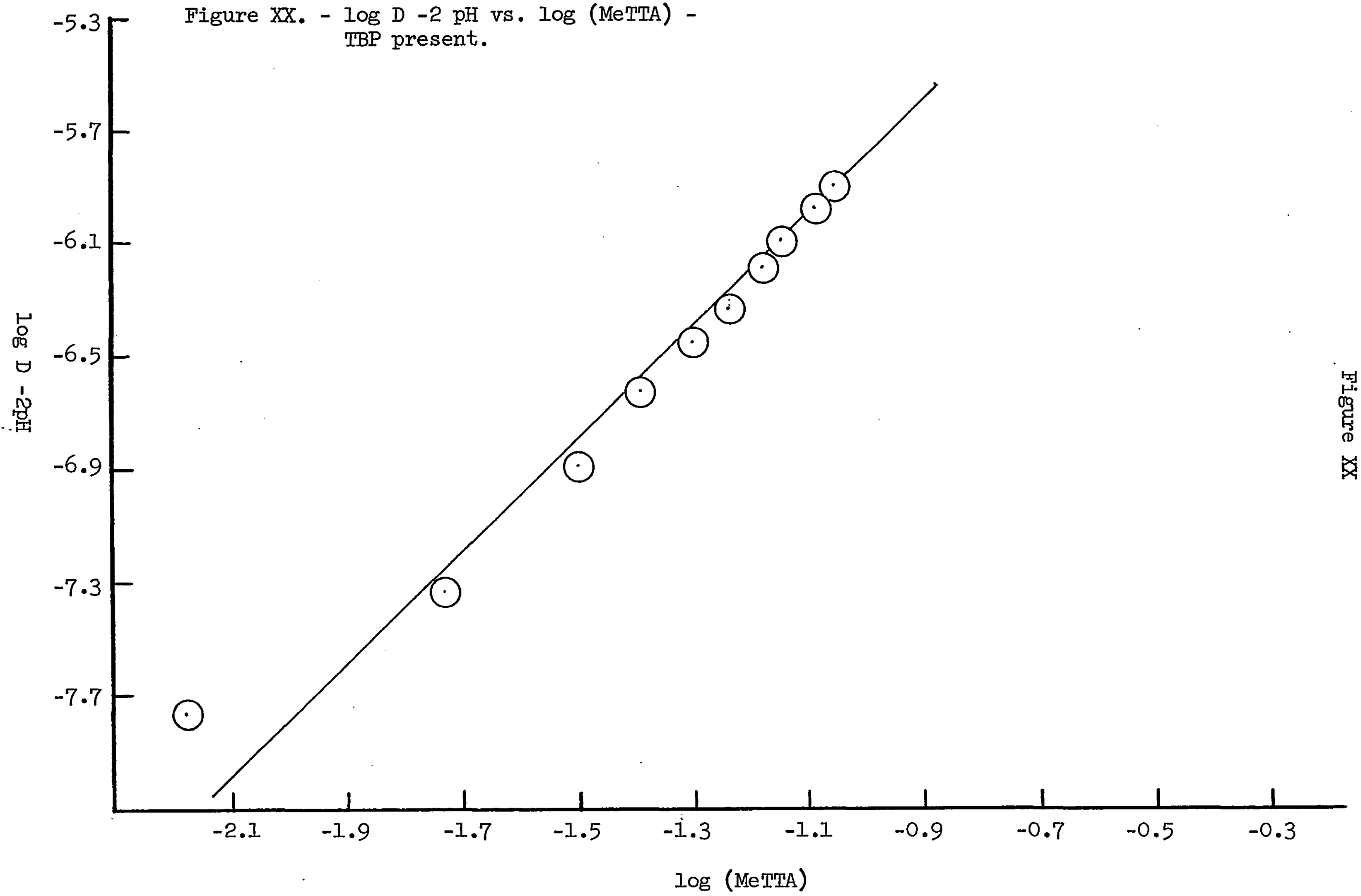

Figure XX. - log D -2 pH vs. log (MeTTA) - TBP present.

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Figure XXI

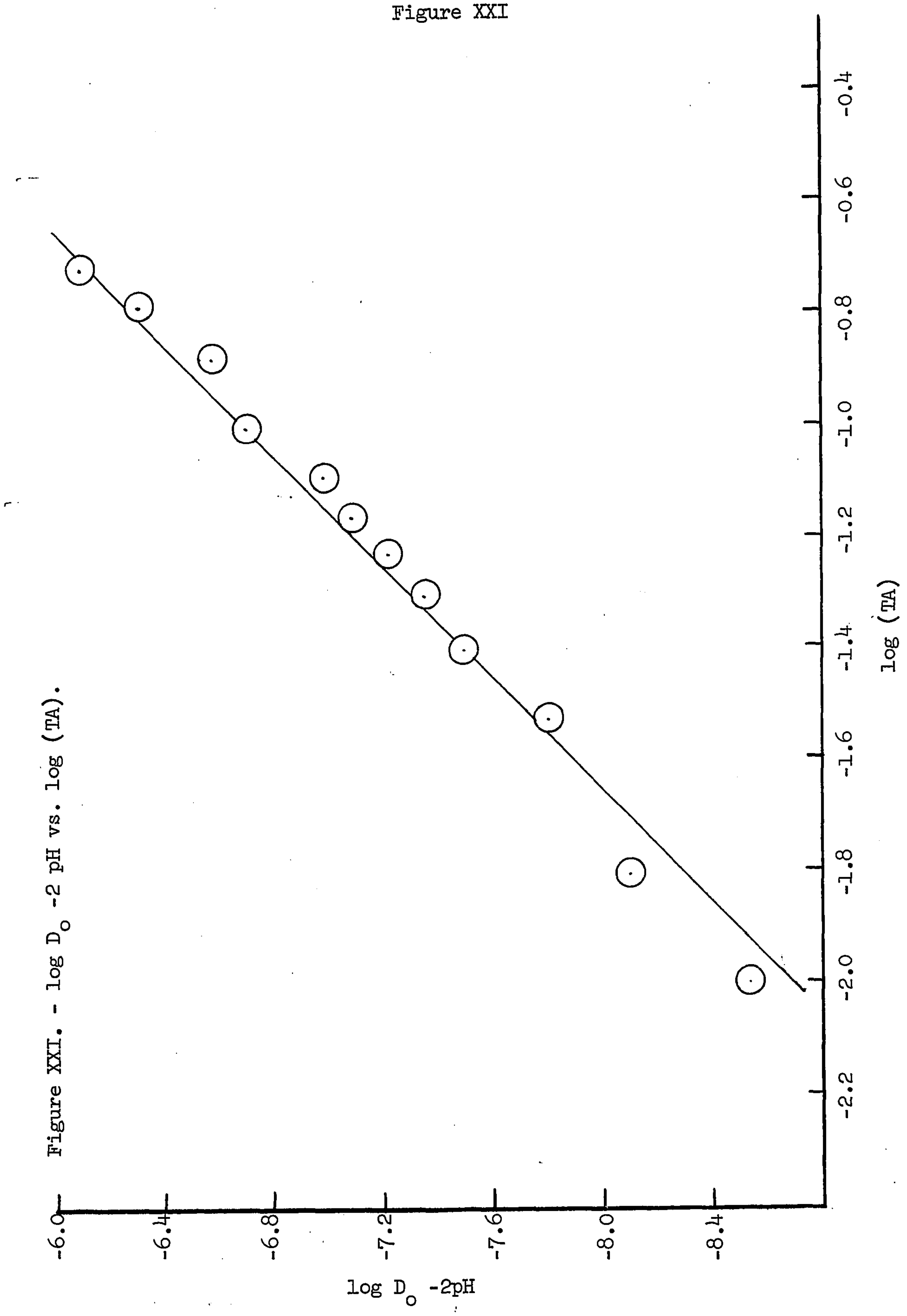

Figure XXI. - log D_o -2 pH vs. log (TA).

Figure XXII

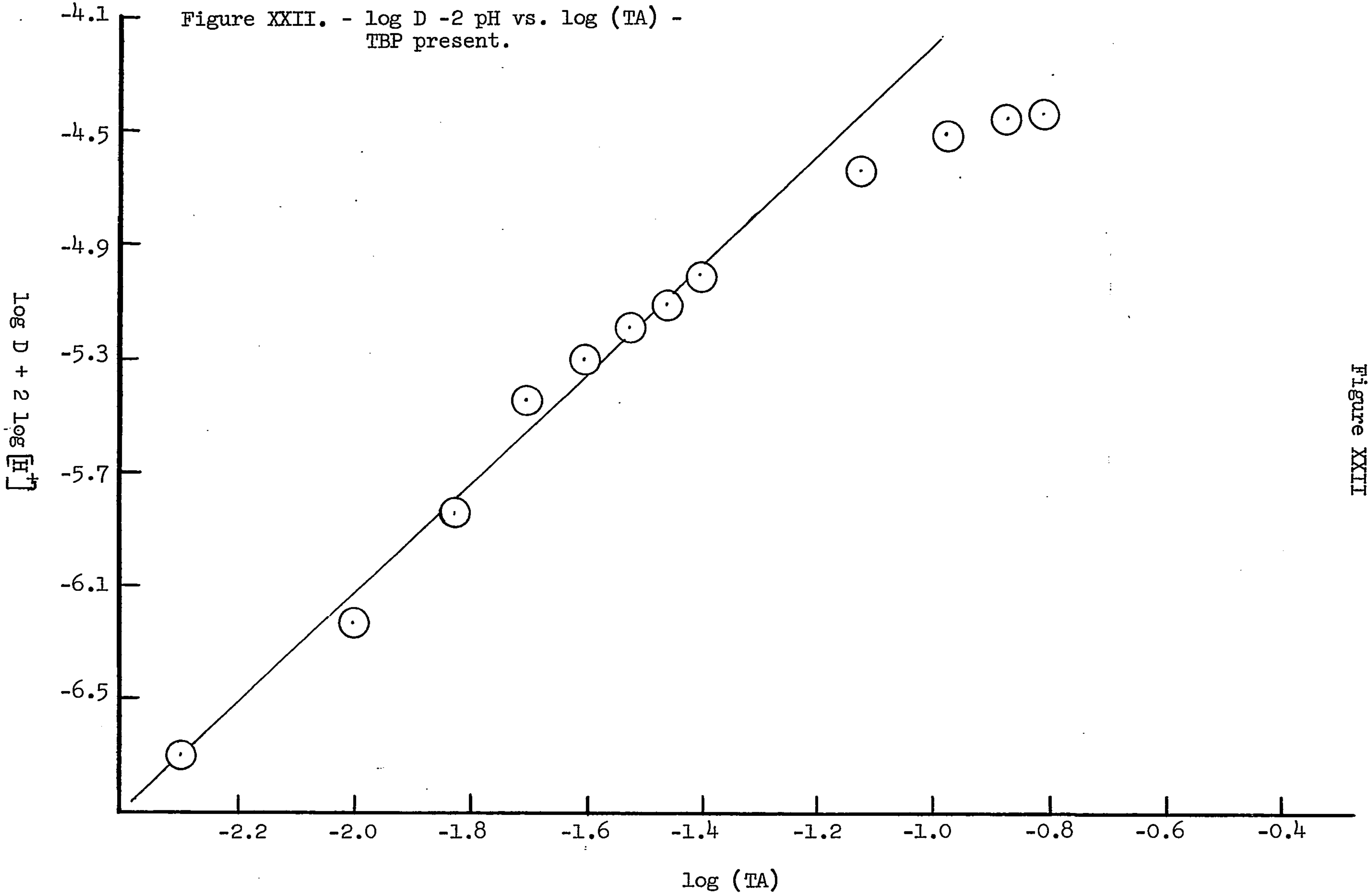

Figure XXII. - log D -2 pH vs. log (TA) -
TBP present.

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Figure XXIII

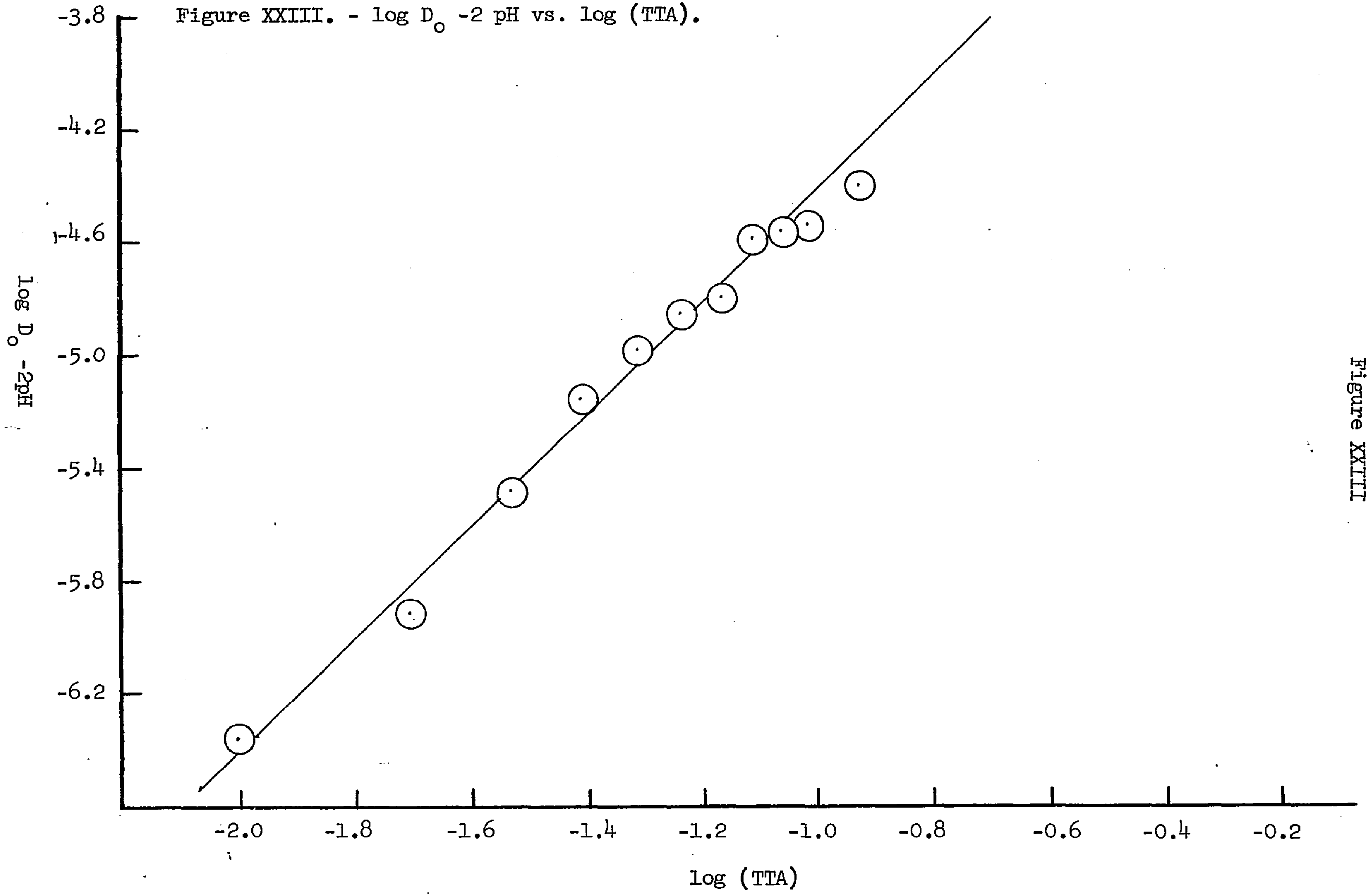

Figure XXIII. - log D_o -2 pH vs. log (TTA).

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Figure XXIV

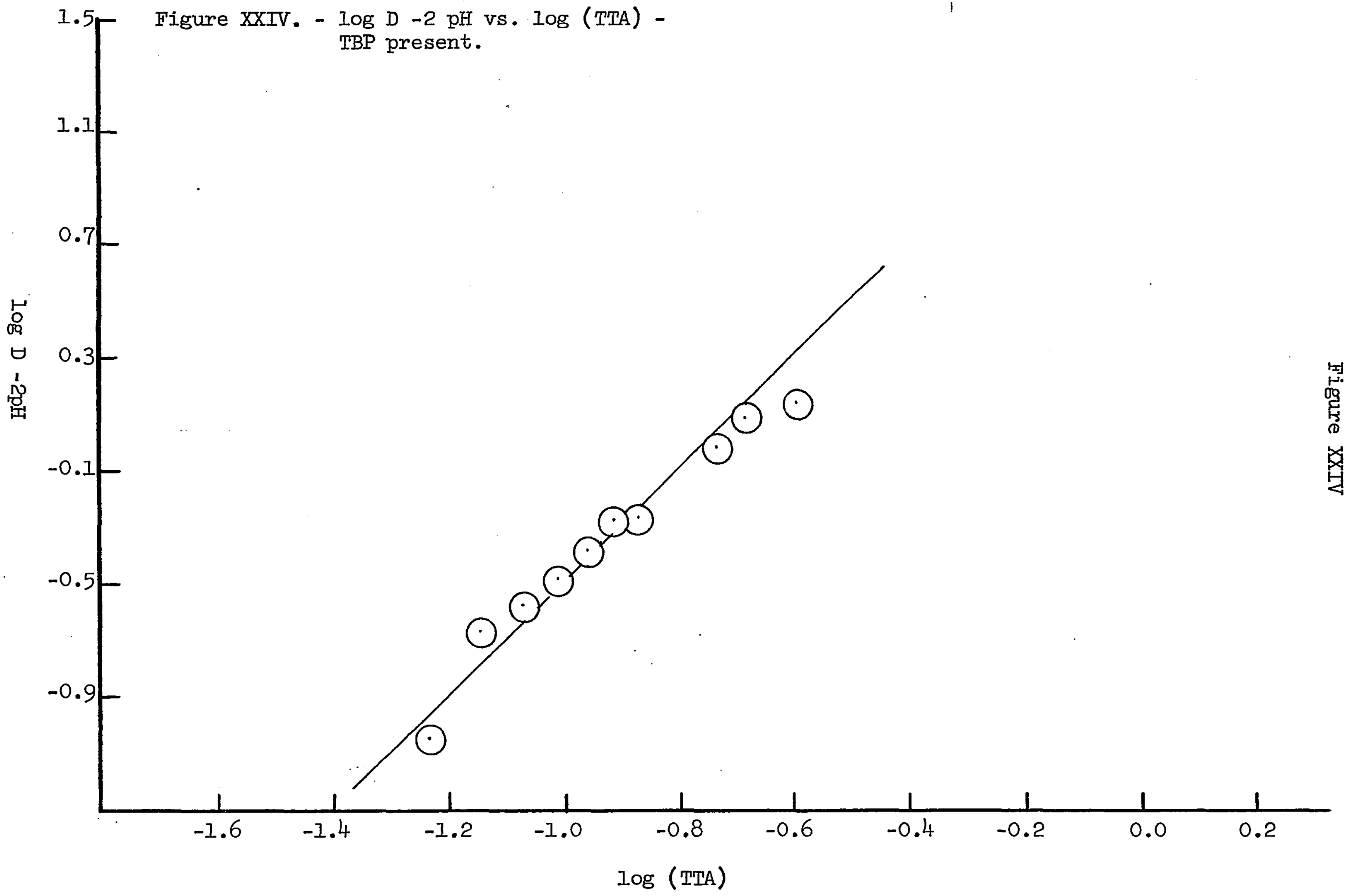

Figure XXIV. - log D -2 pH vs. log (TTA) - TBP present.

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Figure XXV

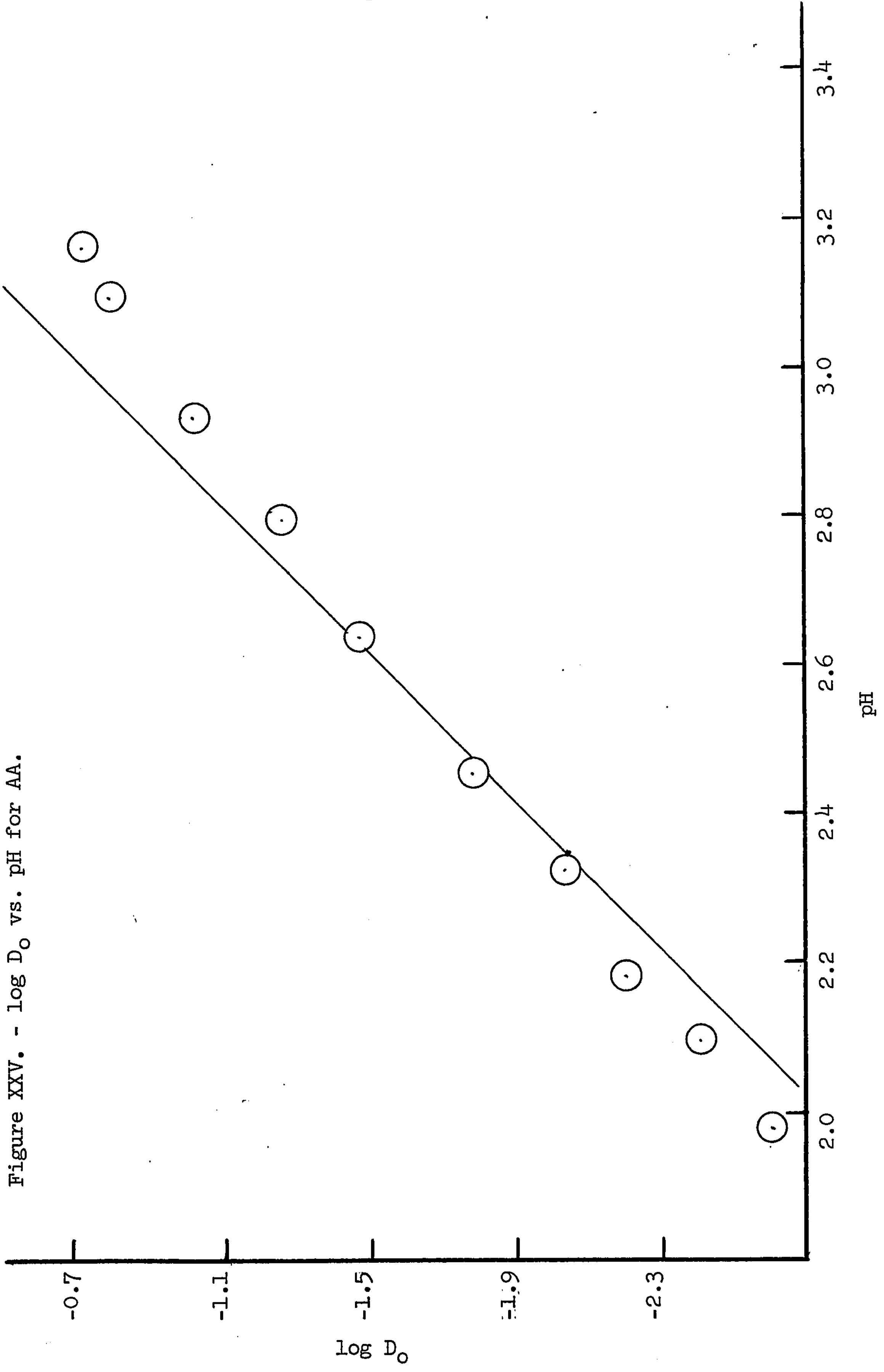

Figure XXV. - log D_o vs. pH for AA.

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Figure XXVI

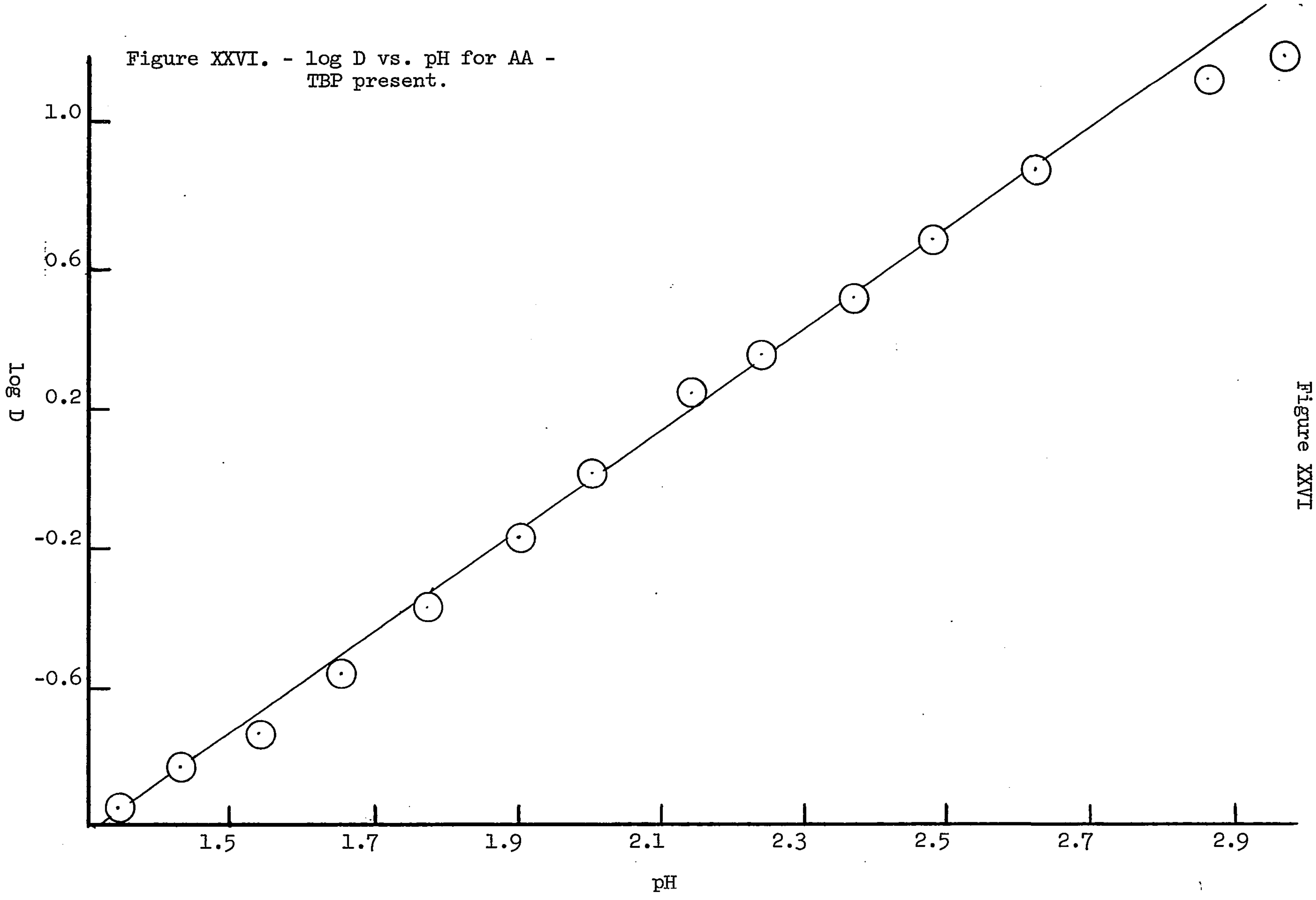

Figure XXVI. - log D vs. pH for AA - TBP present.

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Figure XXVII

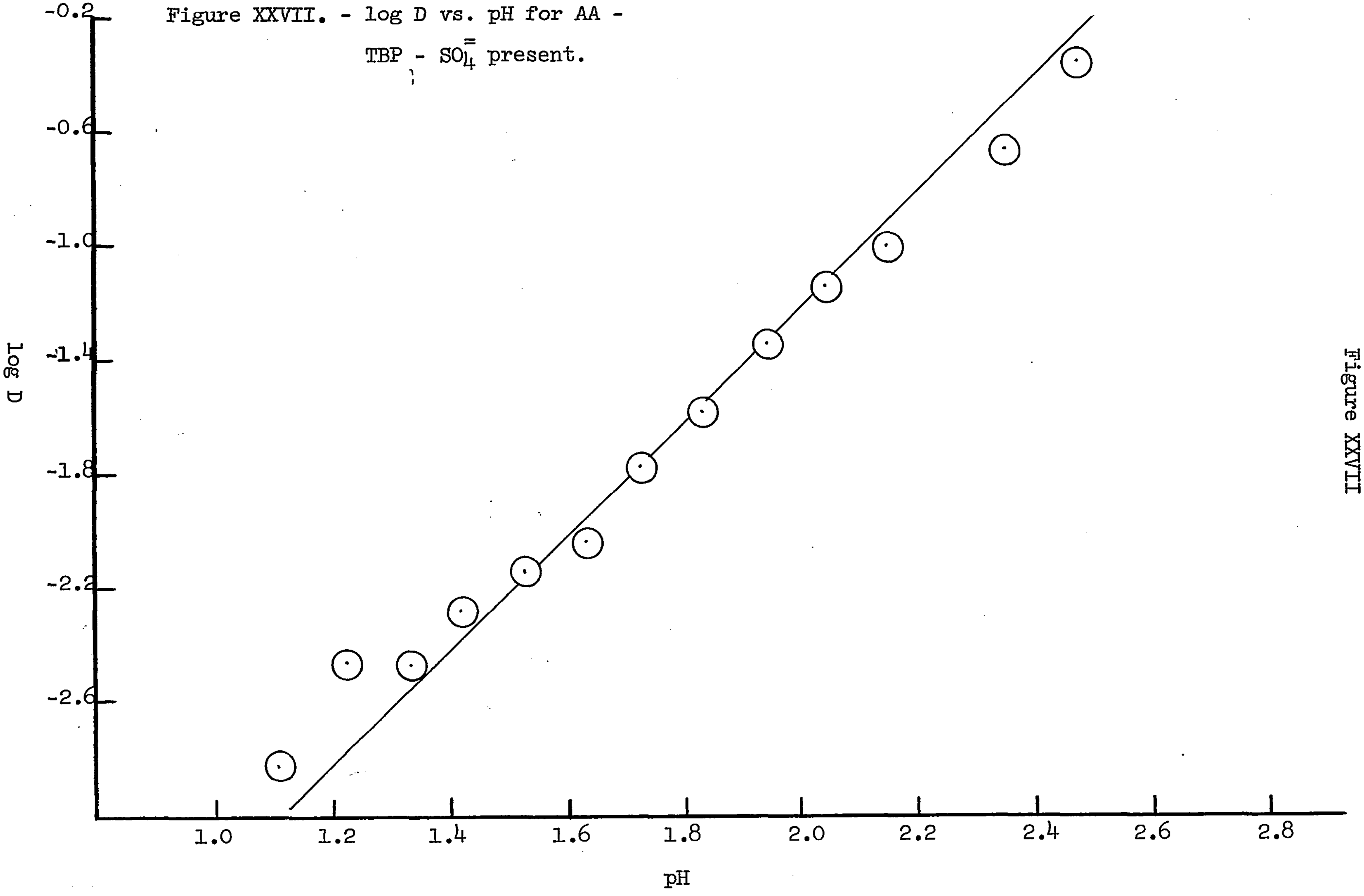

Figure XXVII. - log D vs. pH for AA - TBP - $SO_4^{=}$ present.

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Figure XXVIII

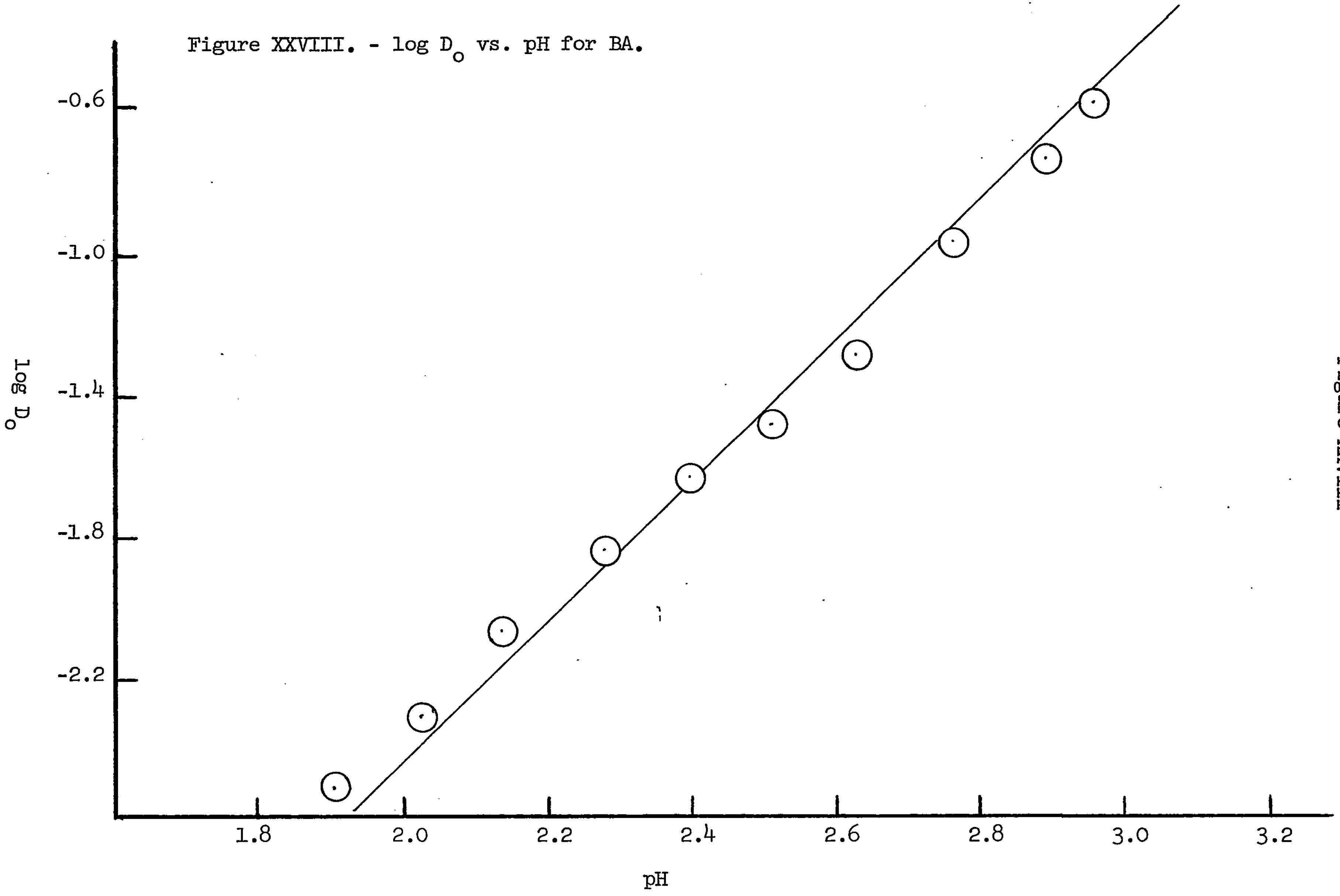

Figure XXVIII. - log D_o vs. pH for BA.

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Figure XXIX

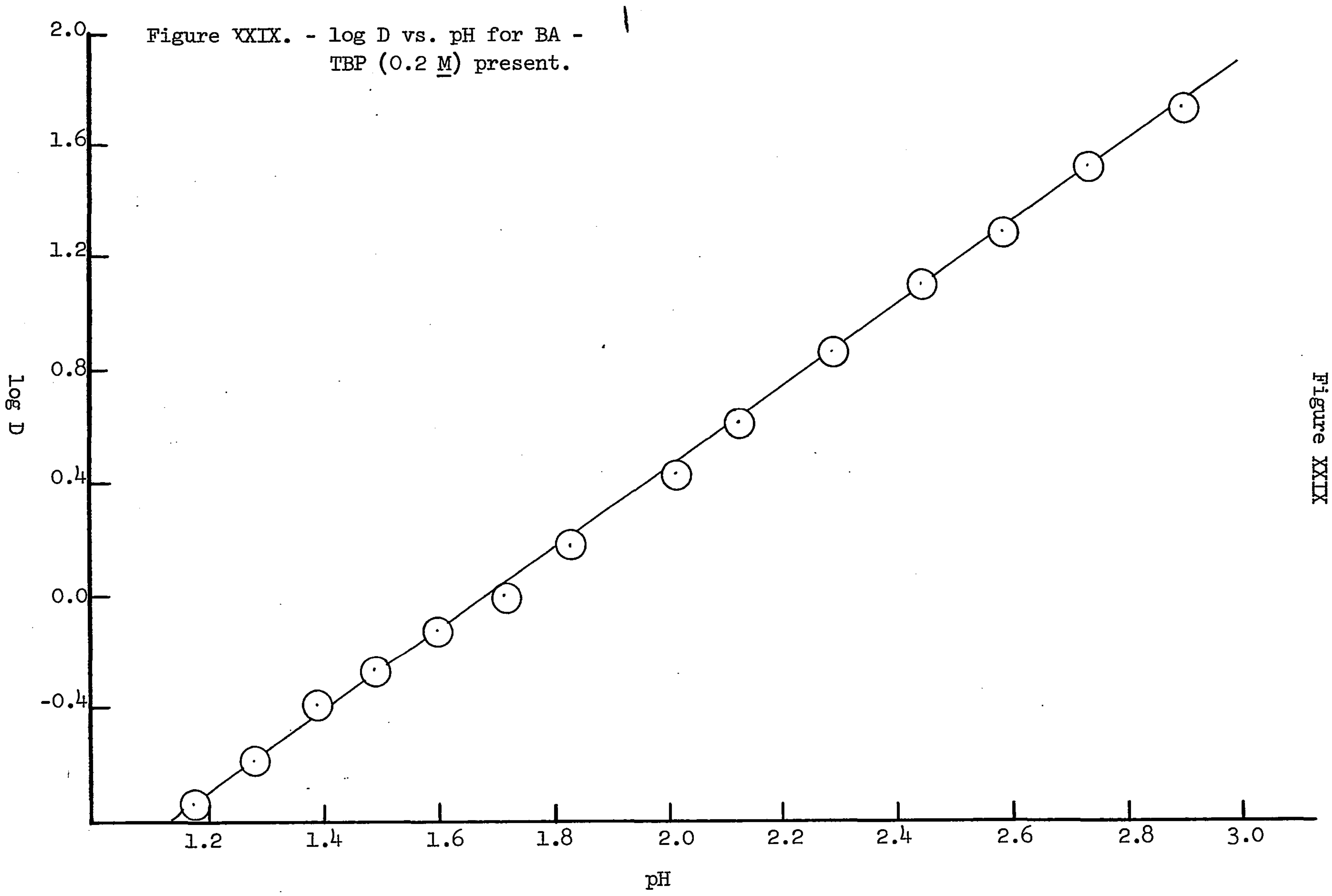

Figure XXIX. - log D vs. pH for BA - TBP (0.2 M) present.

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Figure XXX

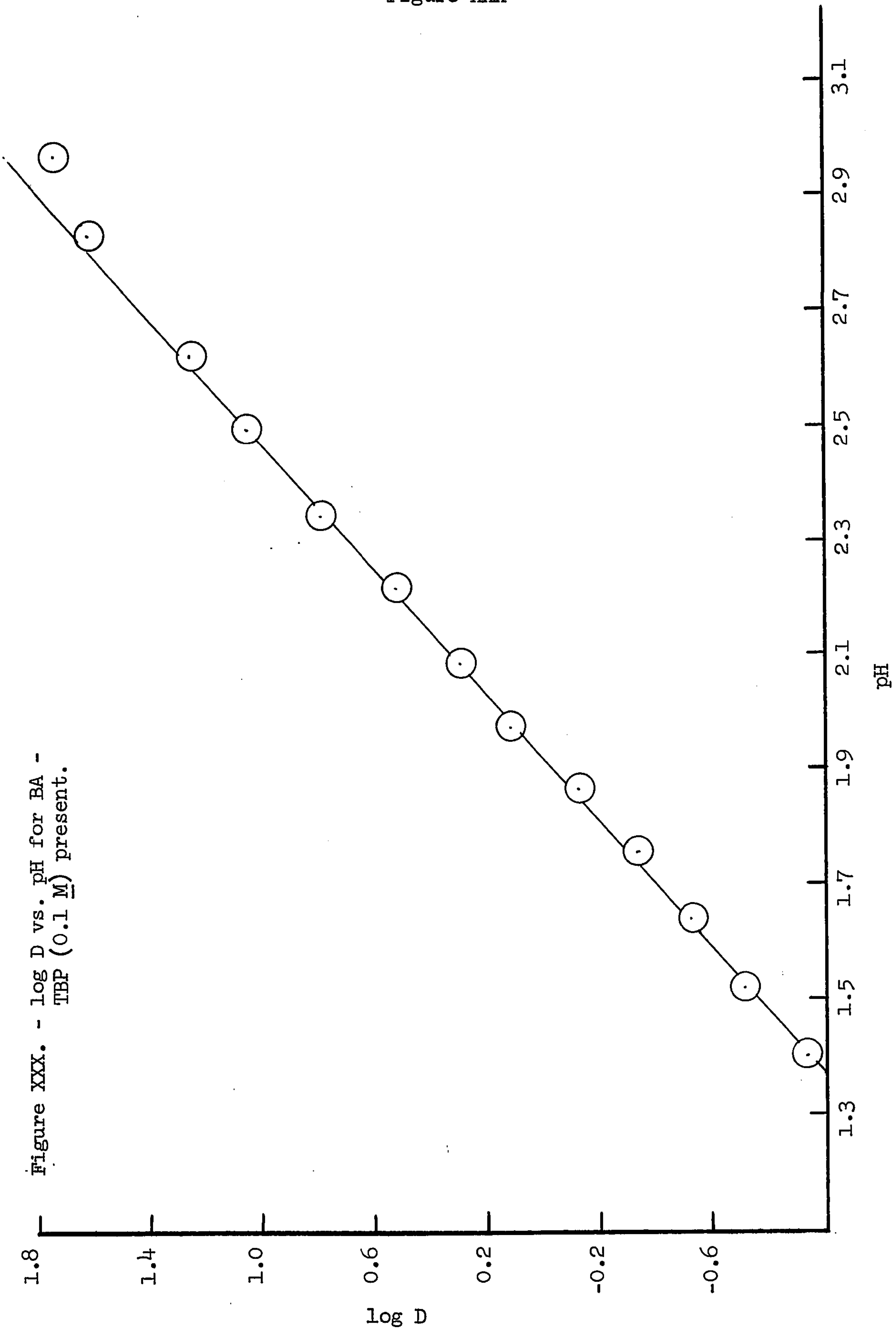

Figure XXX. - log D vs. pH for BA - TBP (0.1 M) present.

Figure XXXI

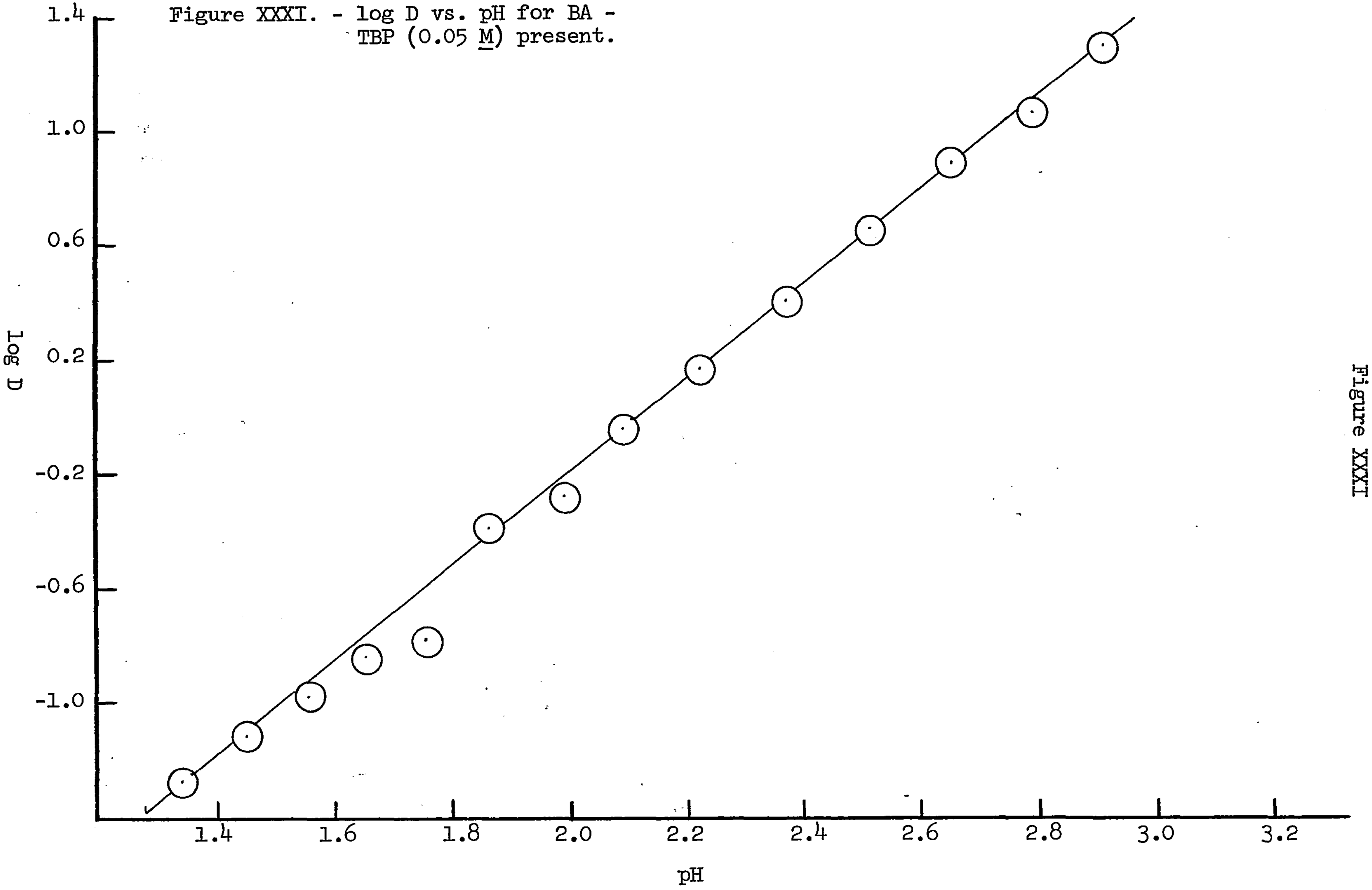

Figure XXXI. - log D vs. pH for BA - TBP (0.05 M) present.

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Figure XXXII

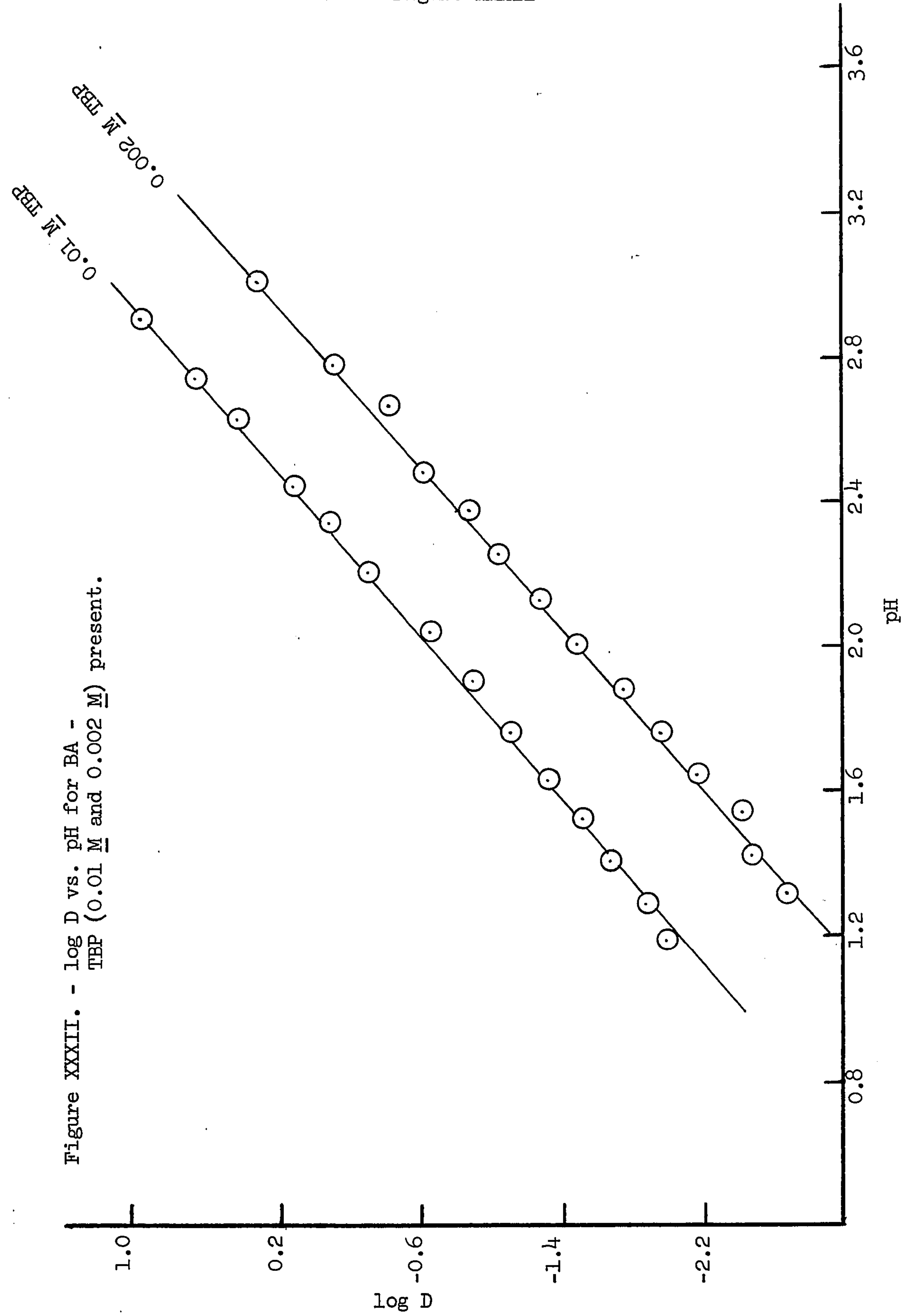

Figure XXXII. - log D vs. pH for BA - TBP (0.01 M and 0.002 M) present.

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Figure XXXIII

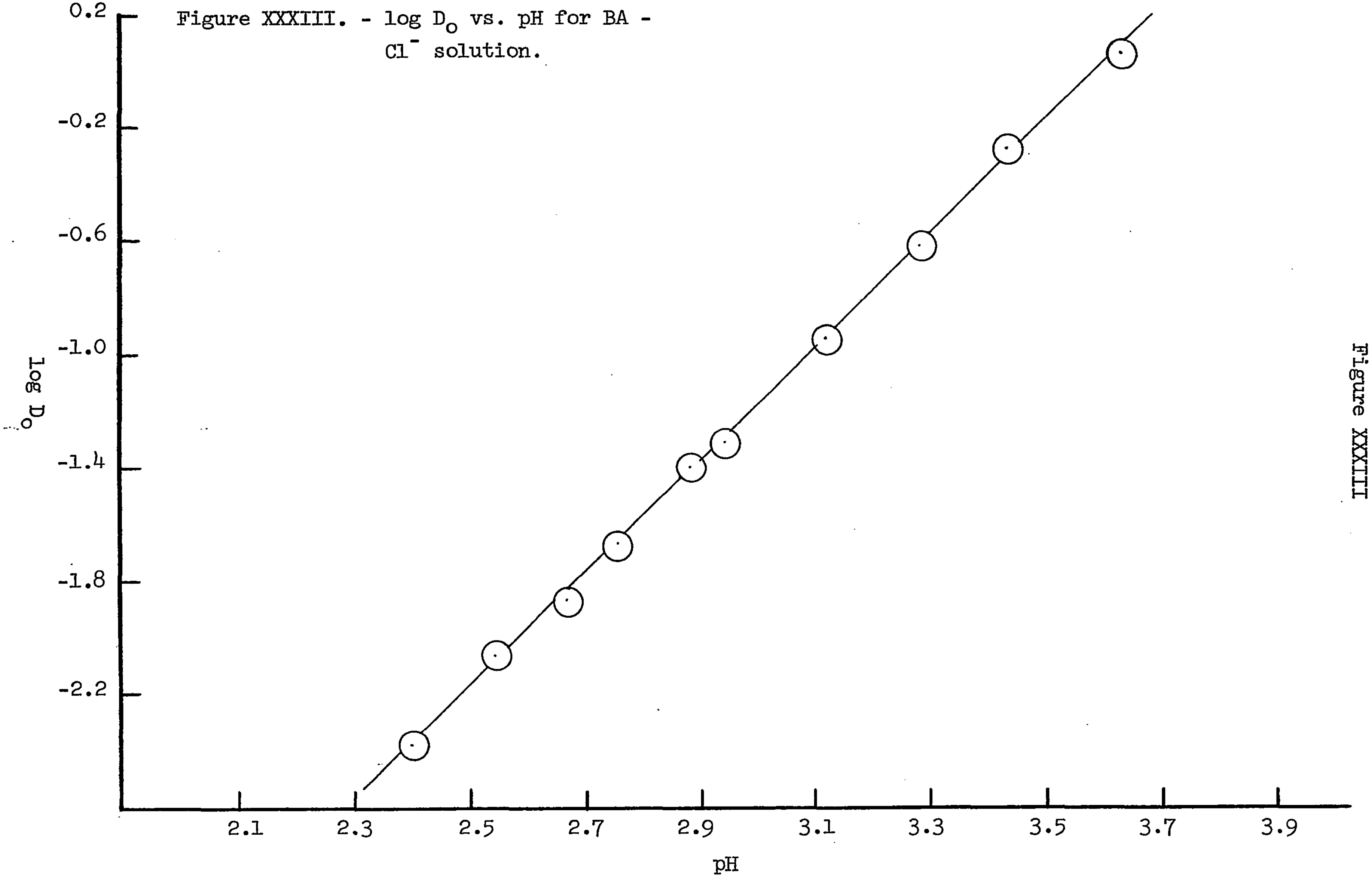

Figure XXXIII. - log D_o vs. pH for BA - Cl^- solution.

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Figure XXXIV

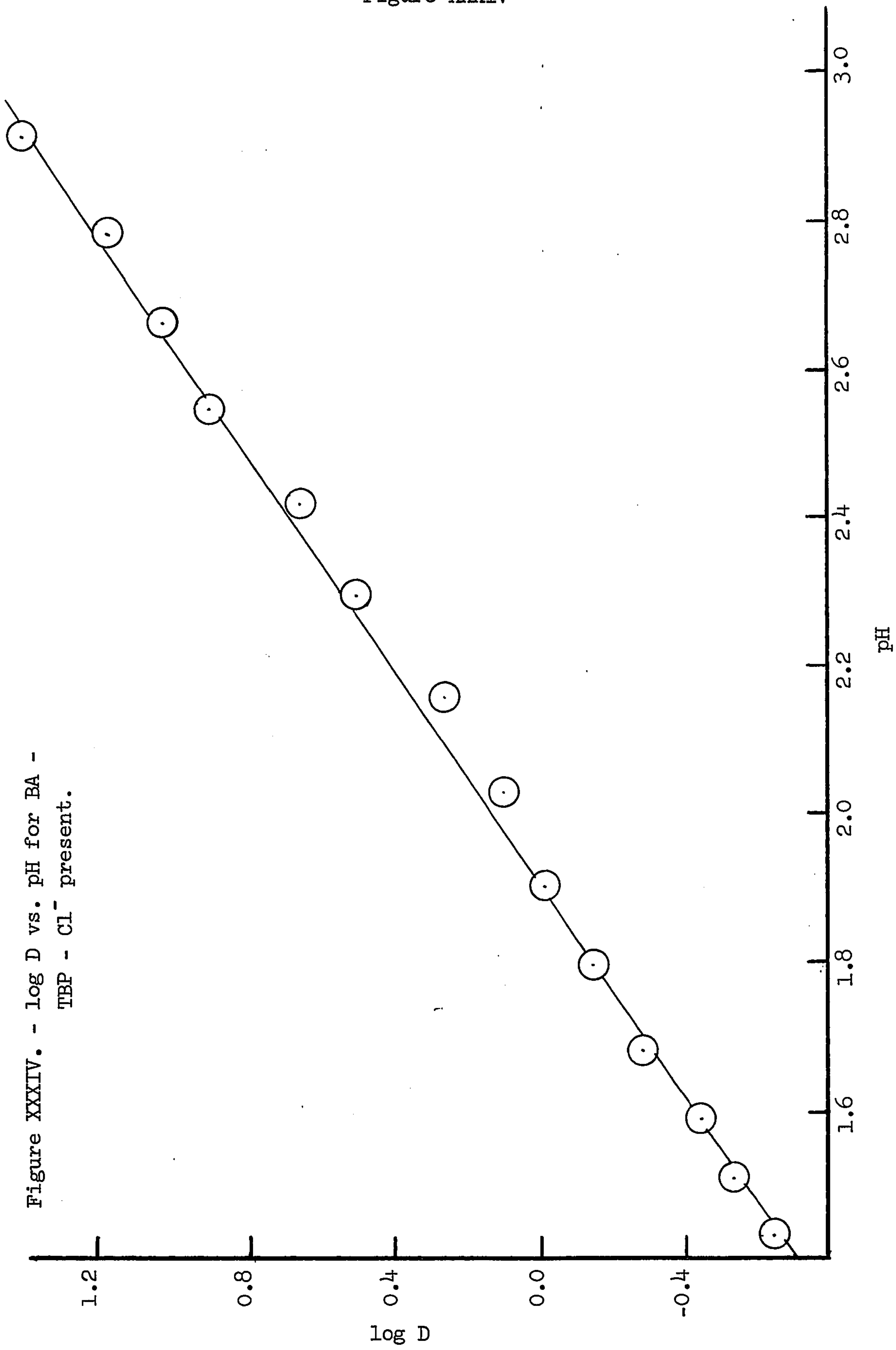

Figure XXXIV. - log D vs. pH for BA - TBP - Cl$^-$ present.

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Figure XXXV

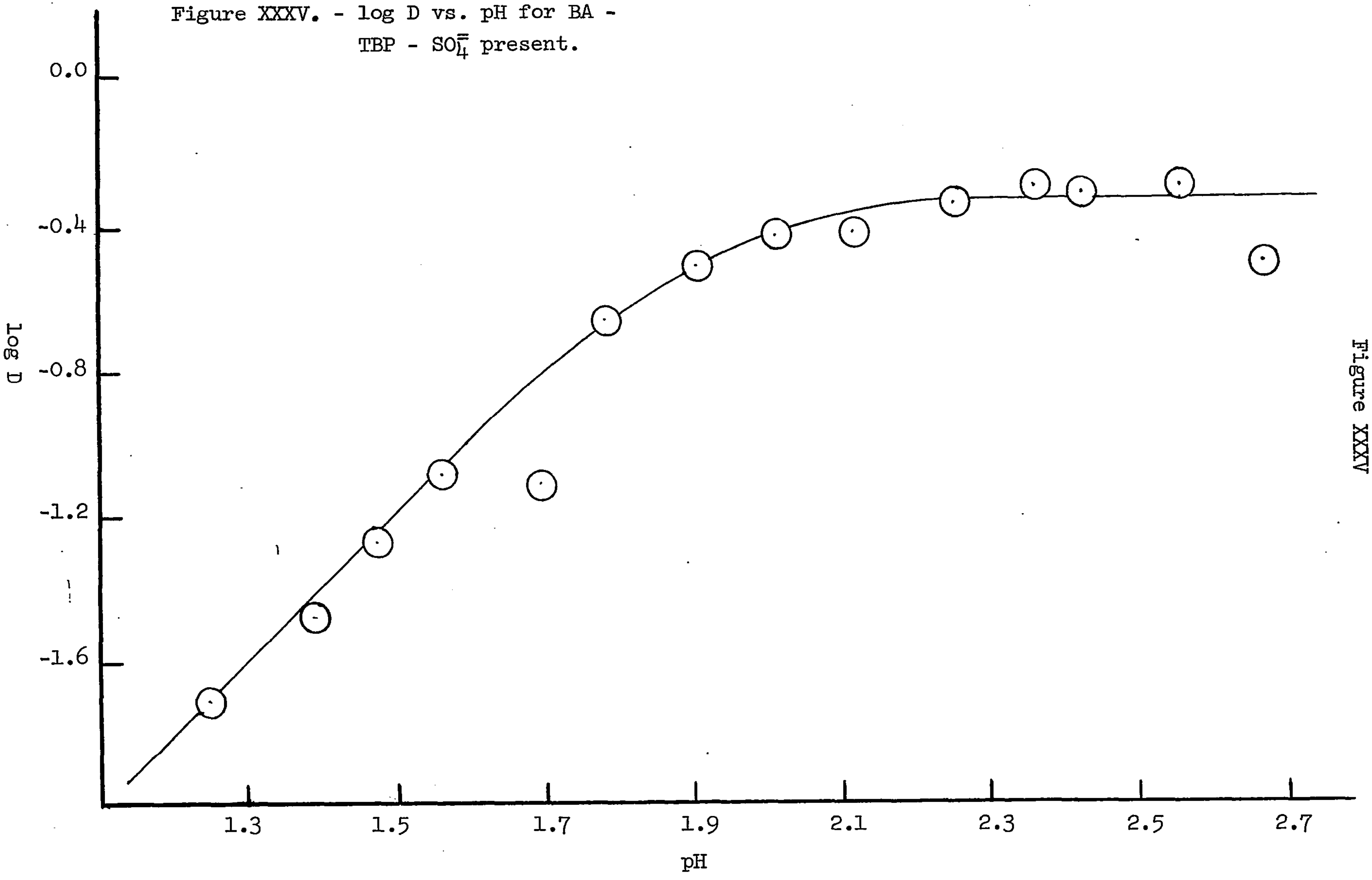

Figure XXXV. - log D vs. pH for BA - TBP - $SO_4^{=}$ present.

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Figure XXXVI

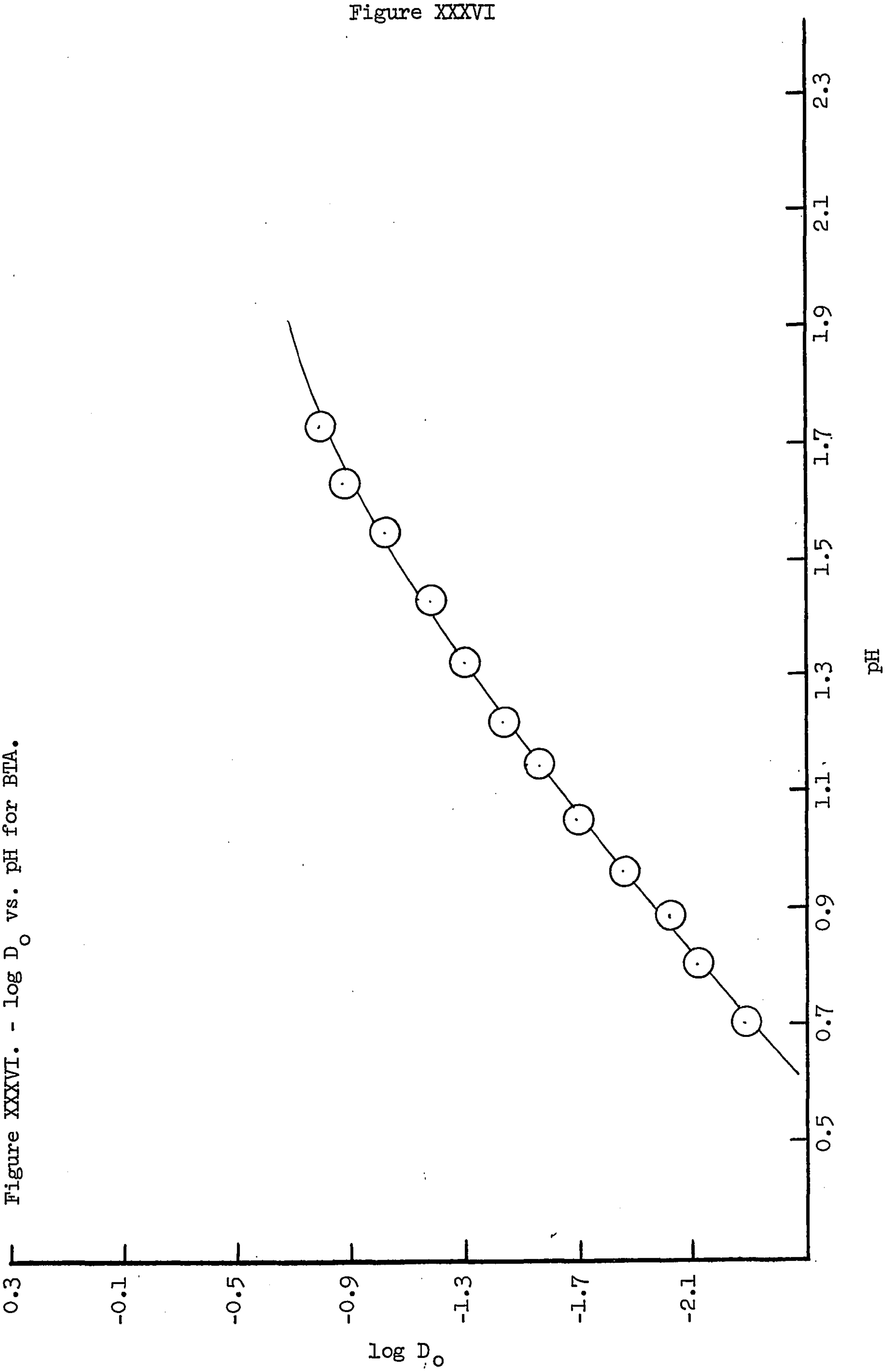

Figure XXXVI. - log D_o vs. pH for BTA.

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Figure XXXVII

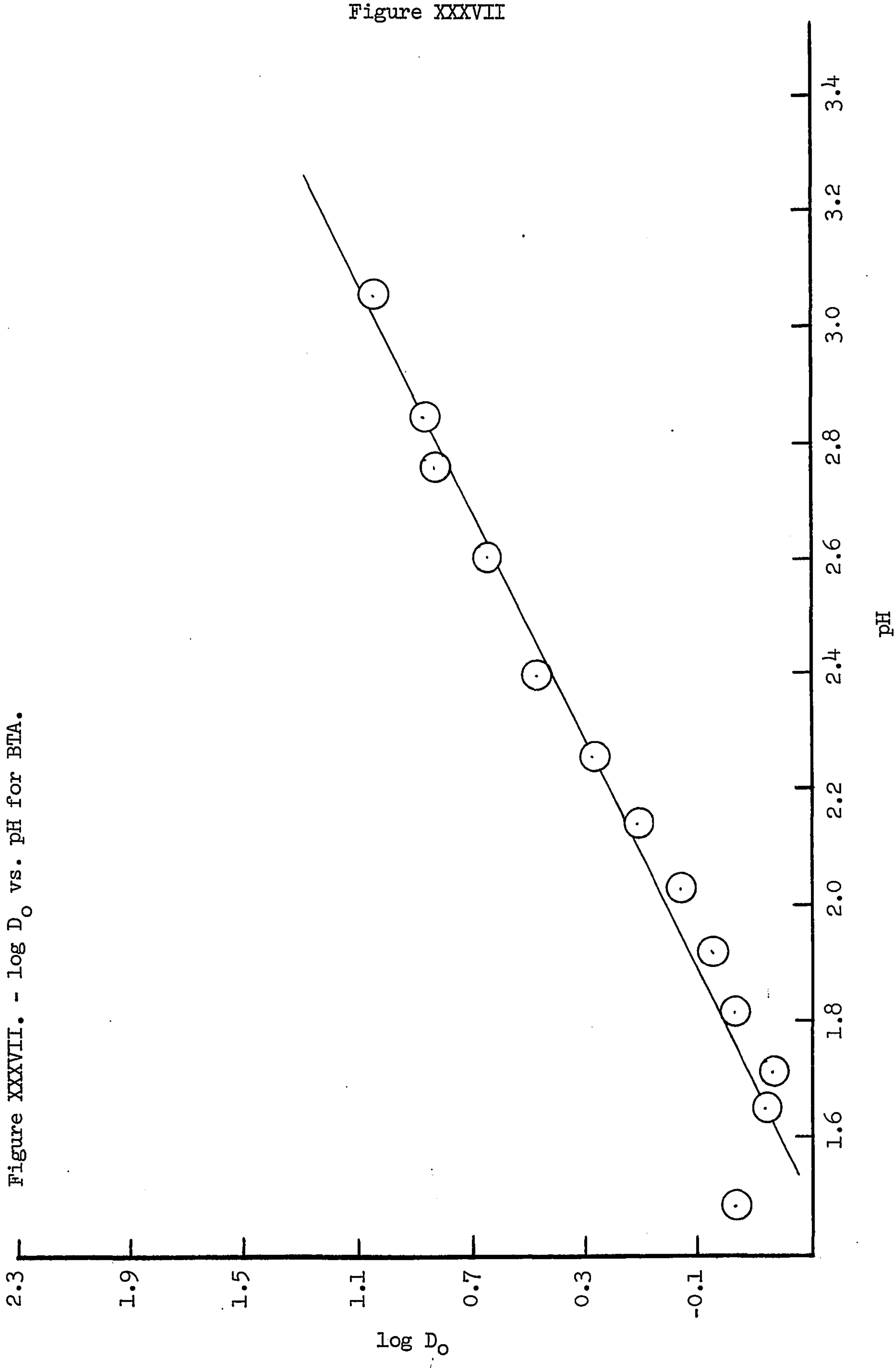

Figure XXXVII. - log D_o vs. pH for BTA.

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Figure XXXVIII

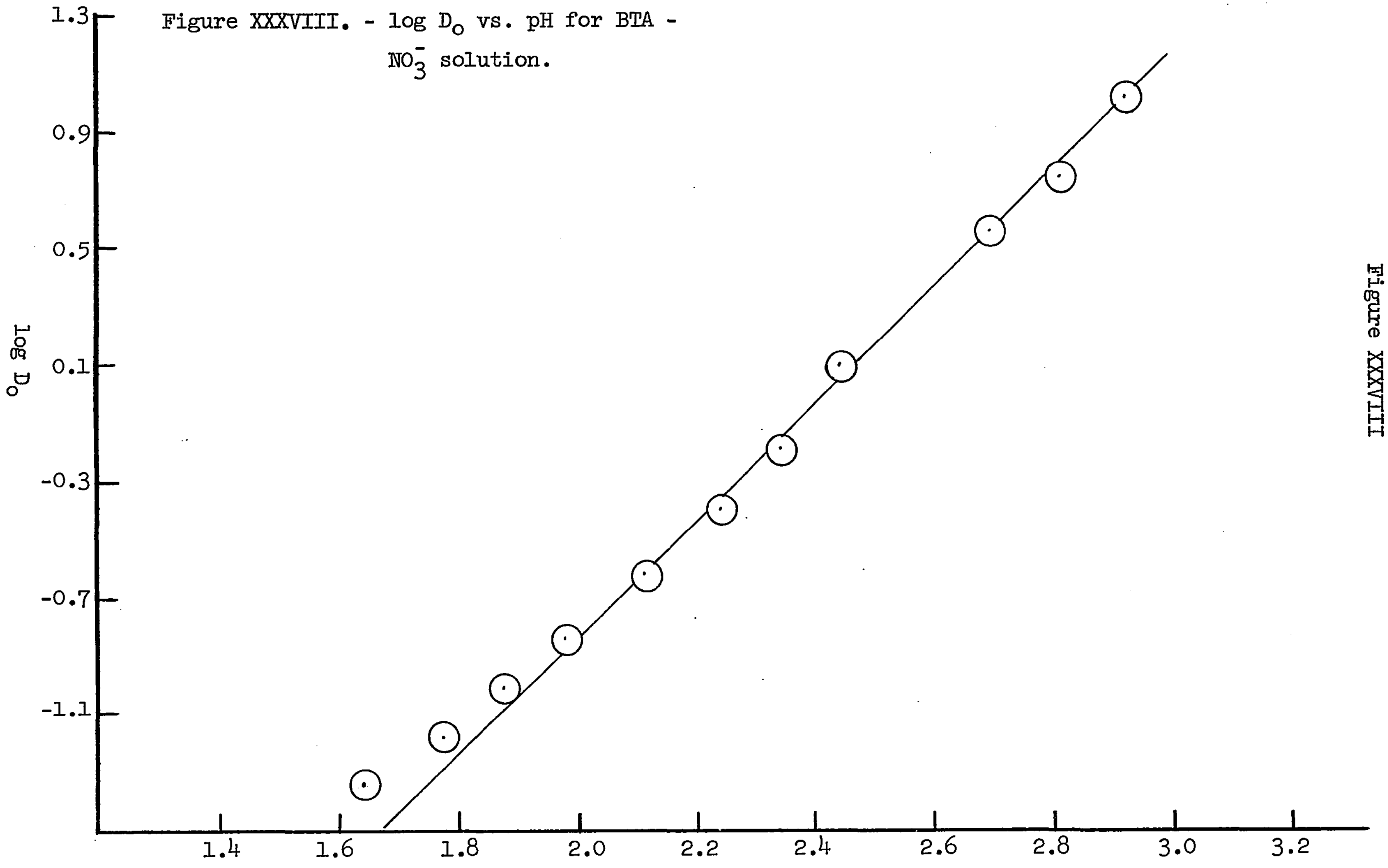

Figure XXXVIII. - log D_o vs. pH for BTA - NO_3^- solution.

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Figure XXXIX

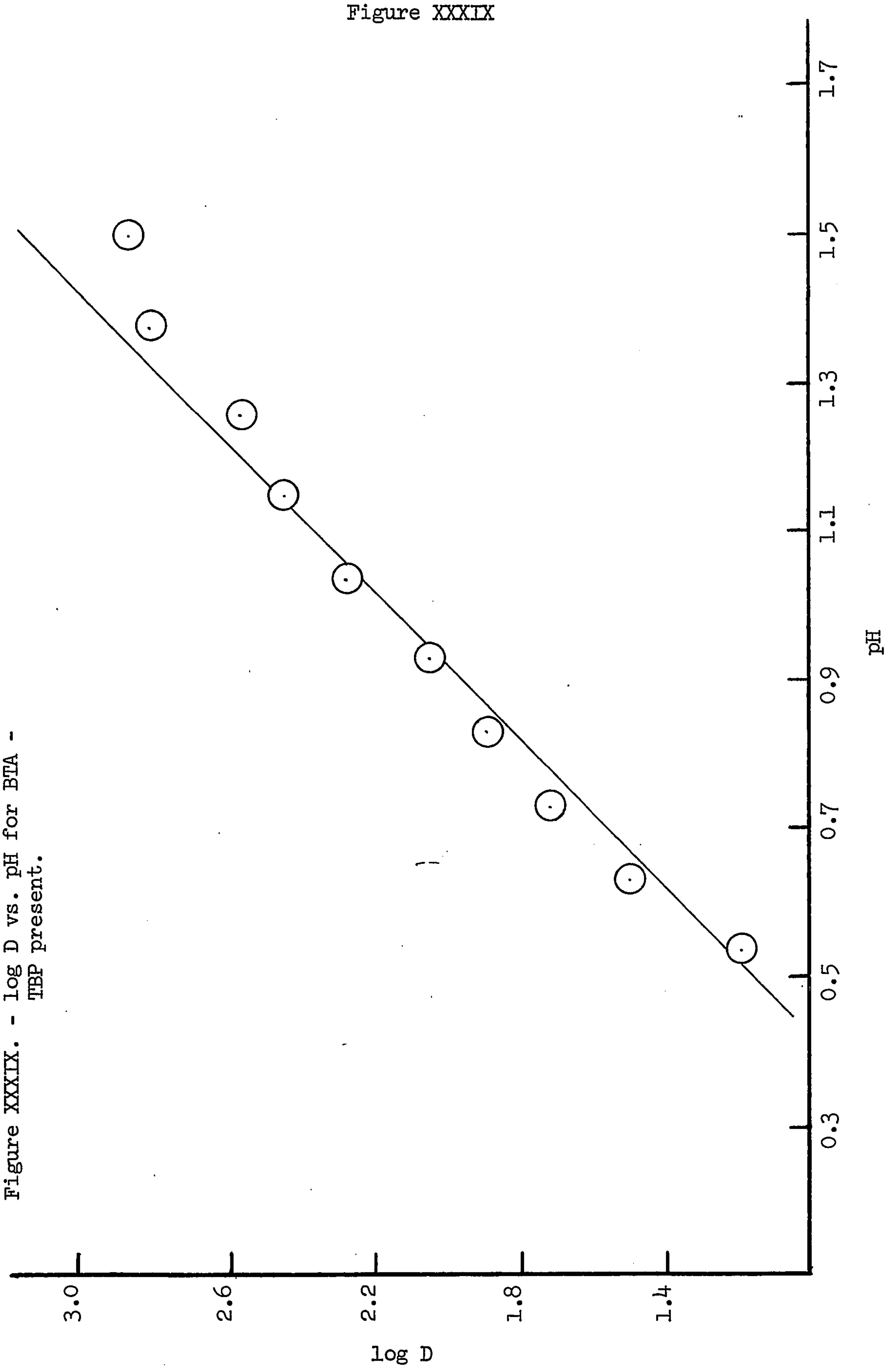

Figure XXXIX. - log D vs. pH for BTA - TBP present.

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Figure XL

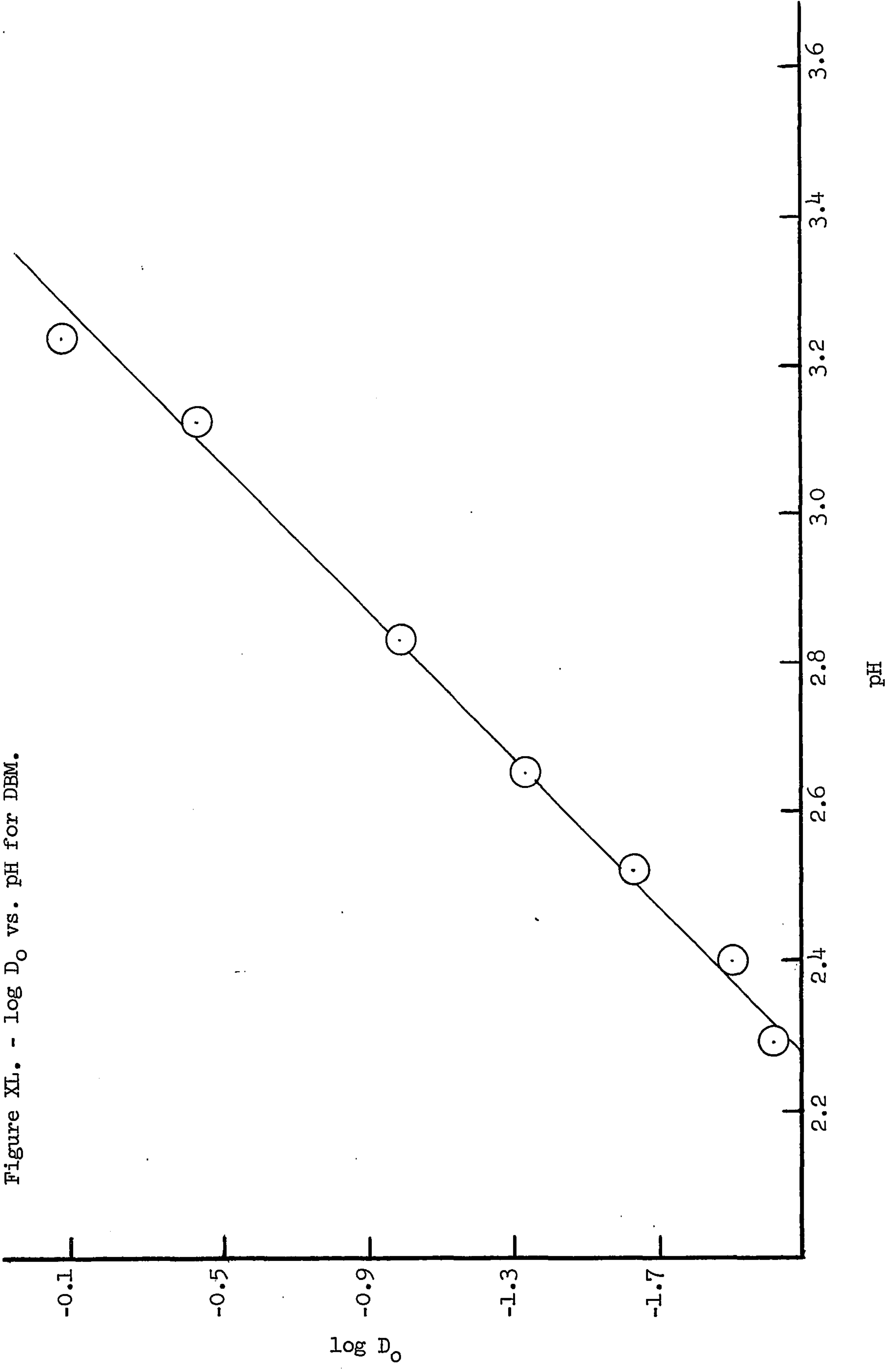

Figure XL. - log D_o vs. pH for DBM.

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Figure XLI

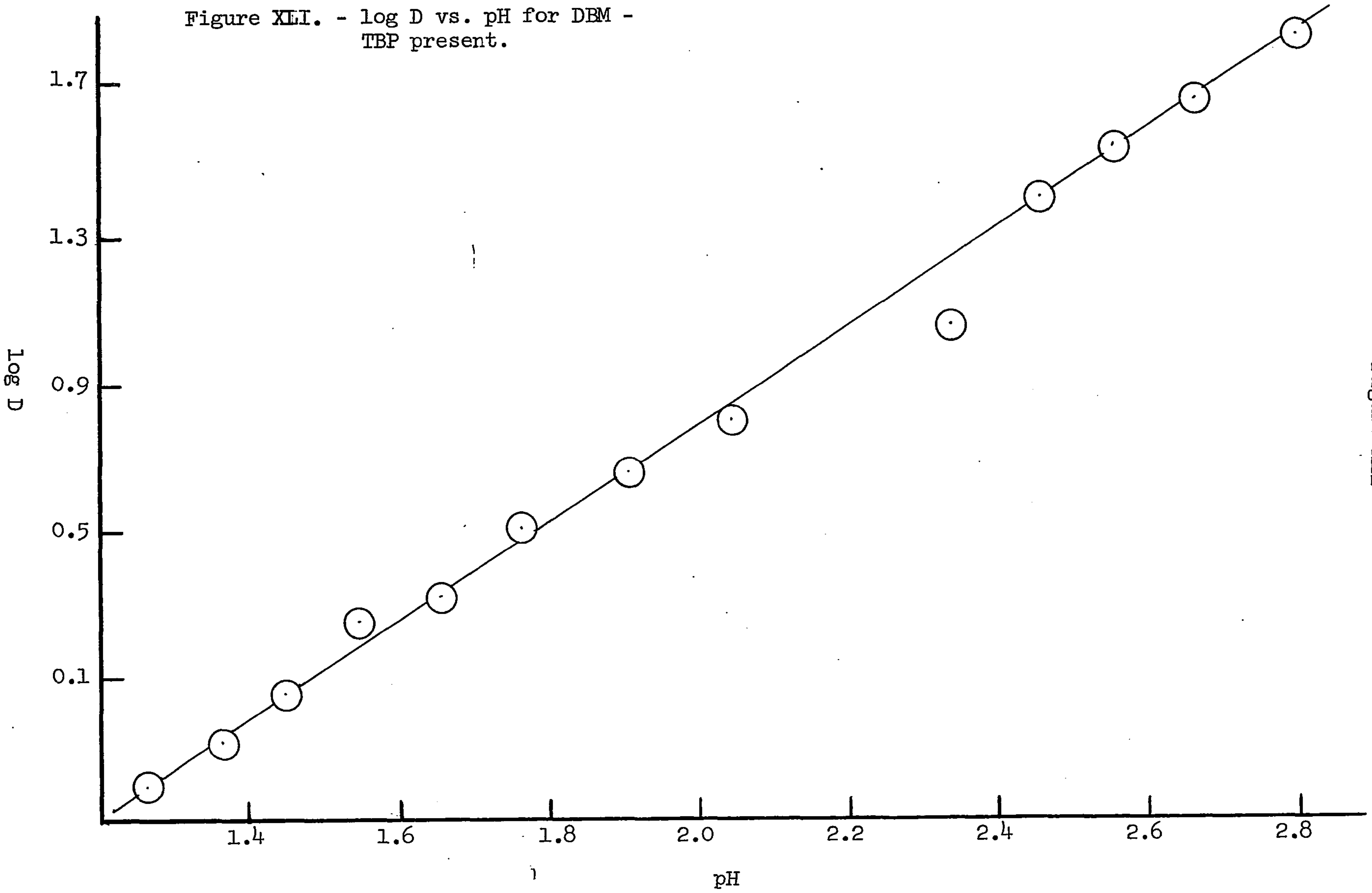

Figure XLI. - log D vs. pH for DBM - TBP present.

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Figure XLII

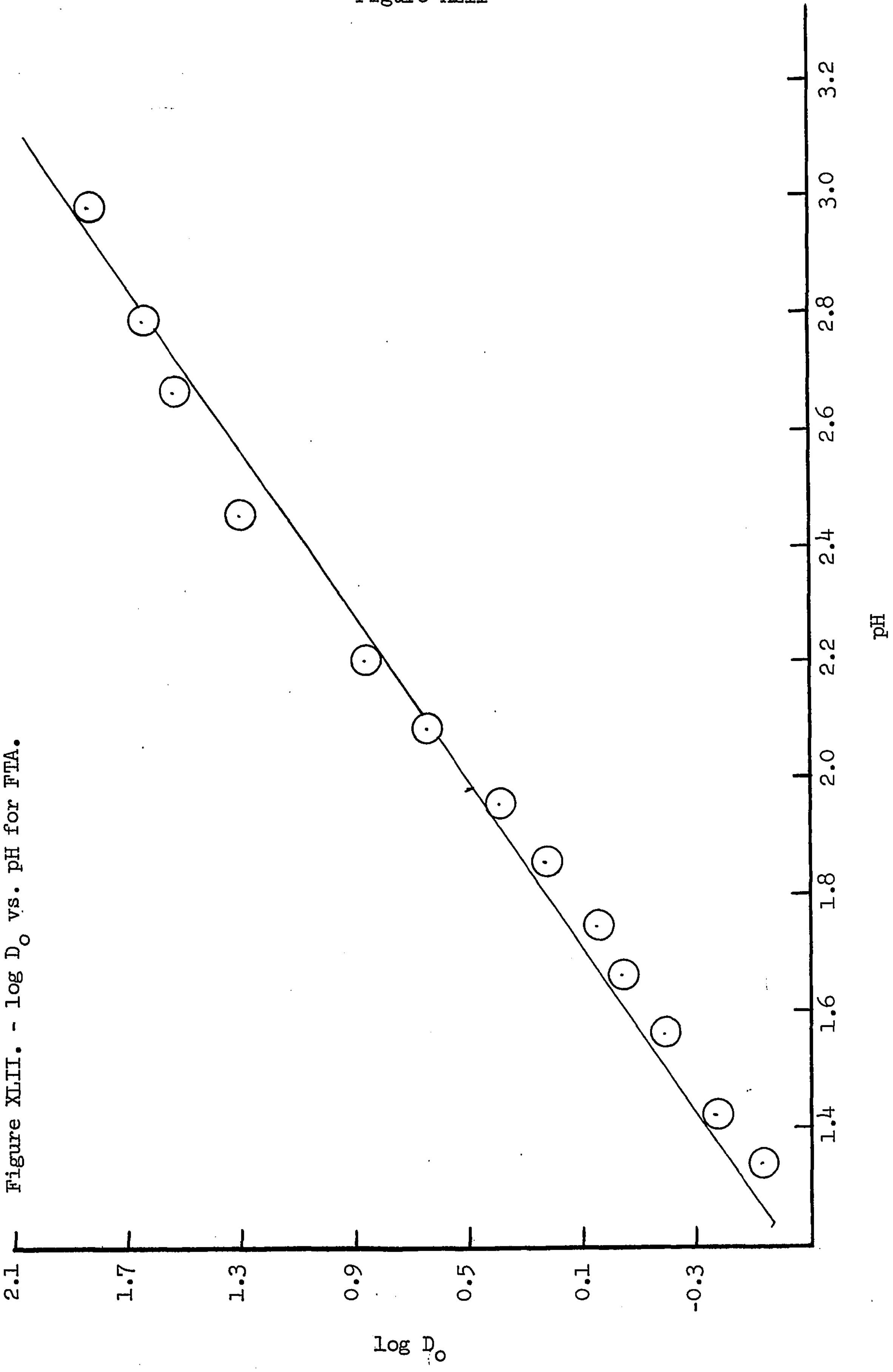

Figure XLII. - log D_o vs. pH for FTA.

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Figure XLIII

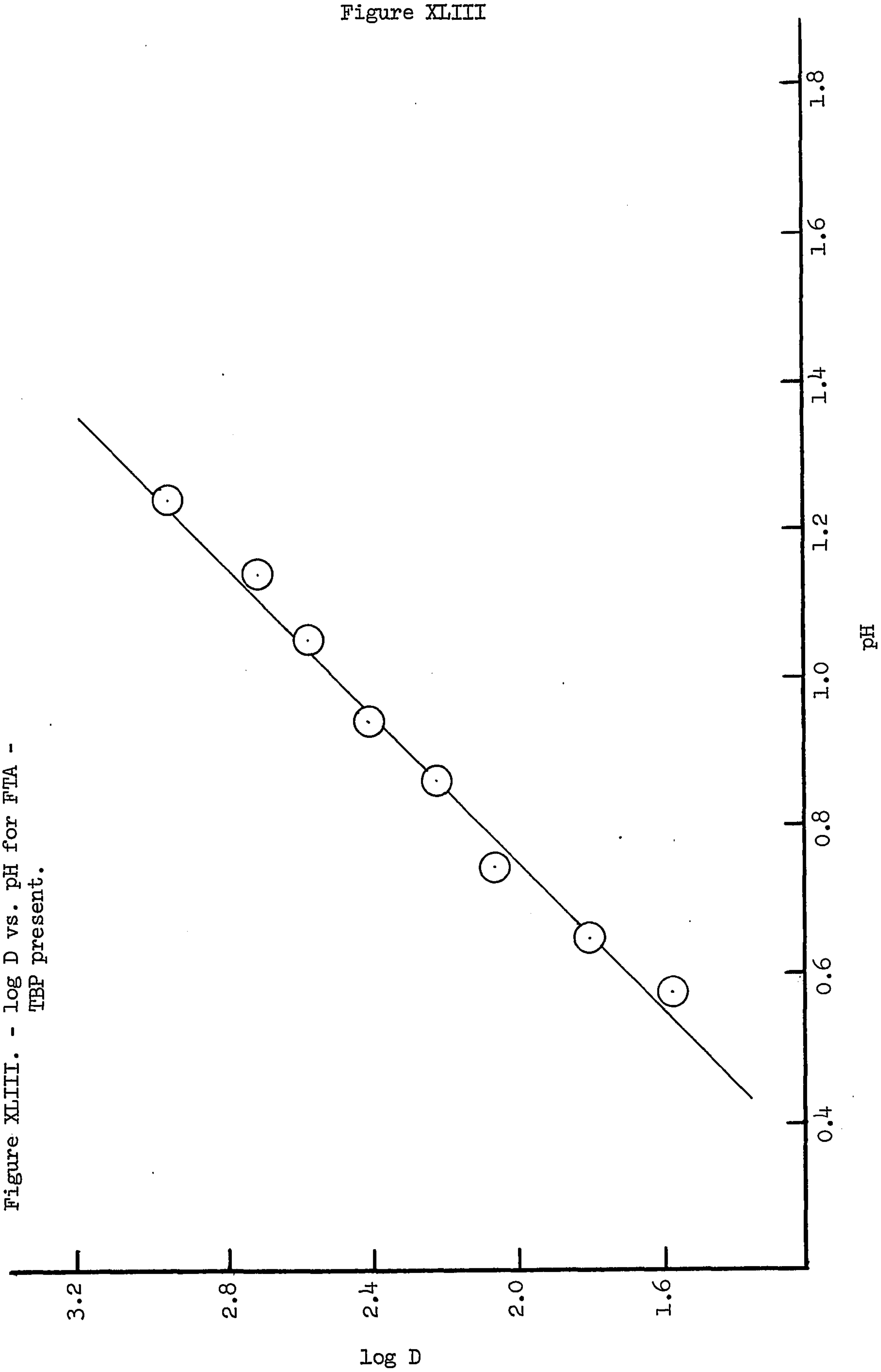

Figure XLIII. - log D vs. pH for FTA - TBP present.

Figure XLIV

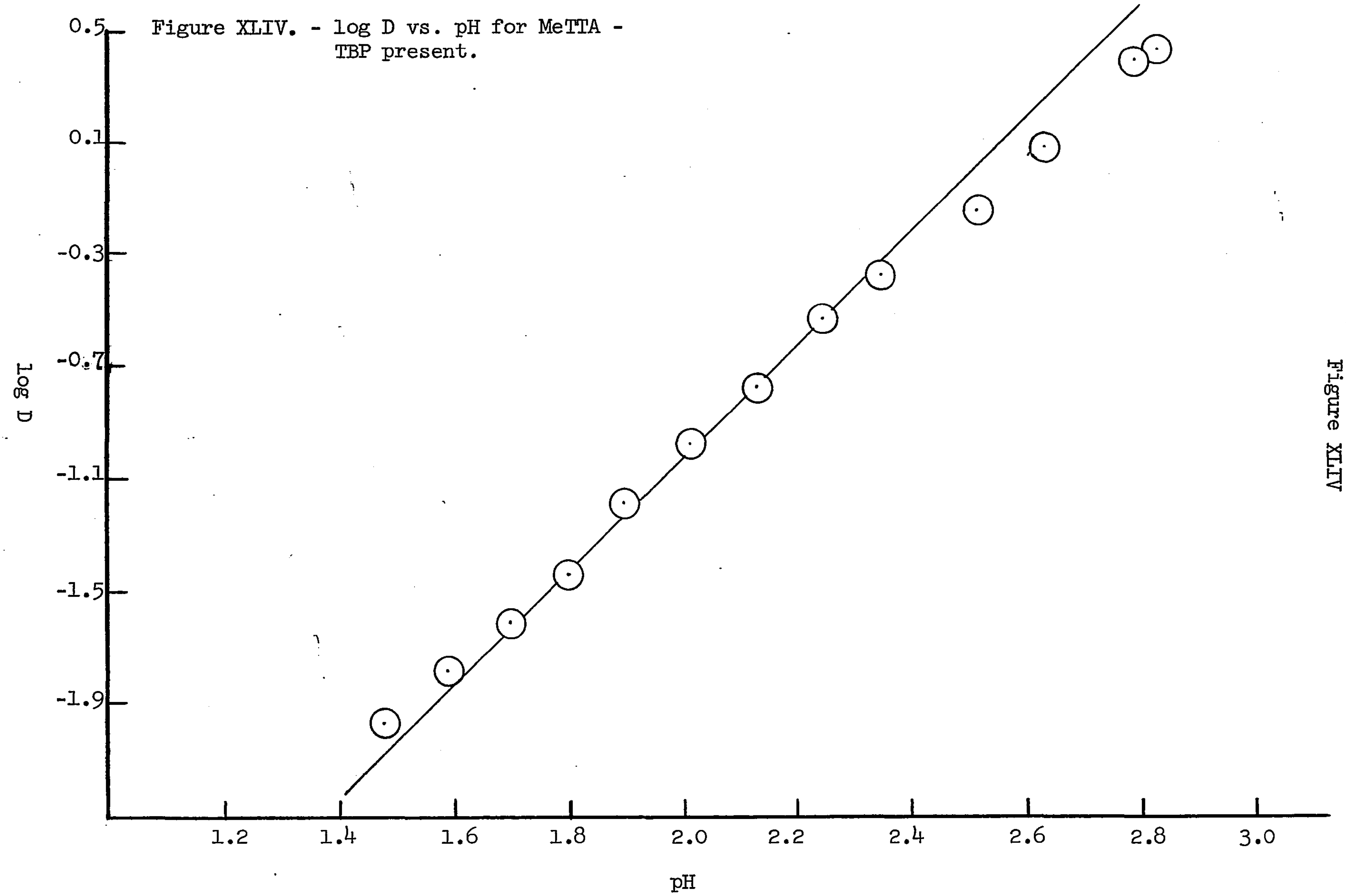

Figure XLIV. - log D vs. pH for MeTTA - TBP present.

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Figure XLV

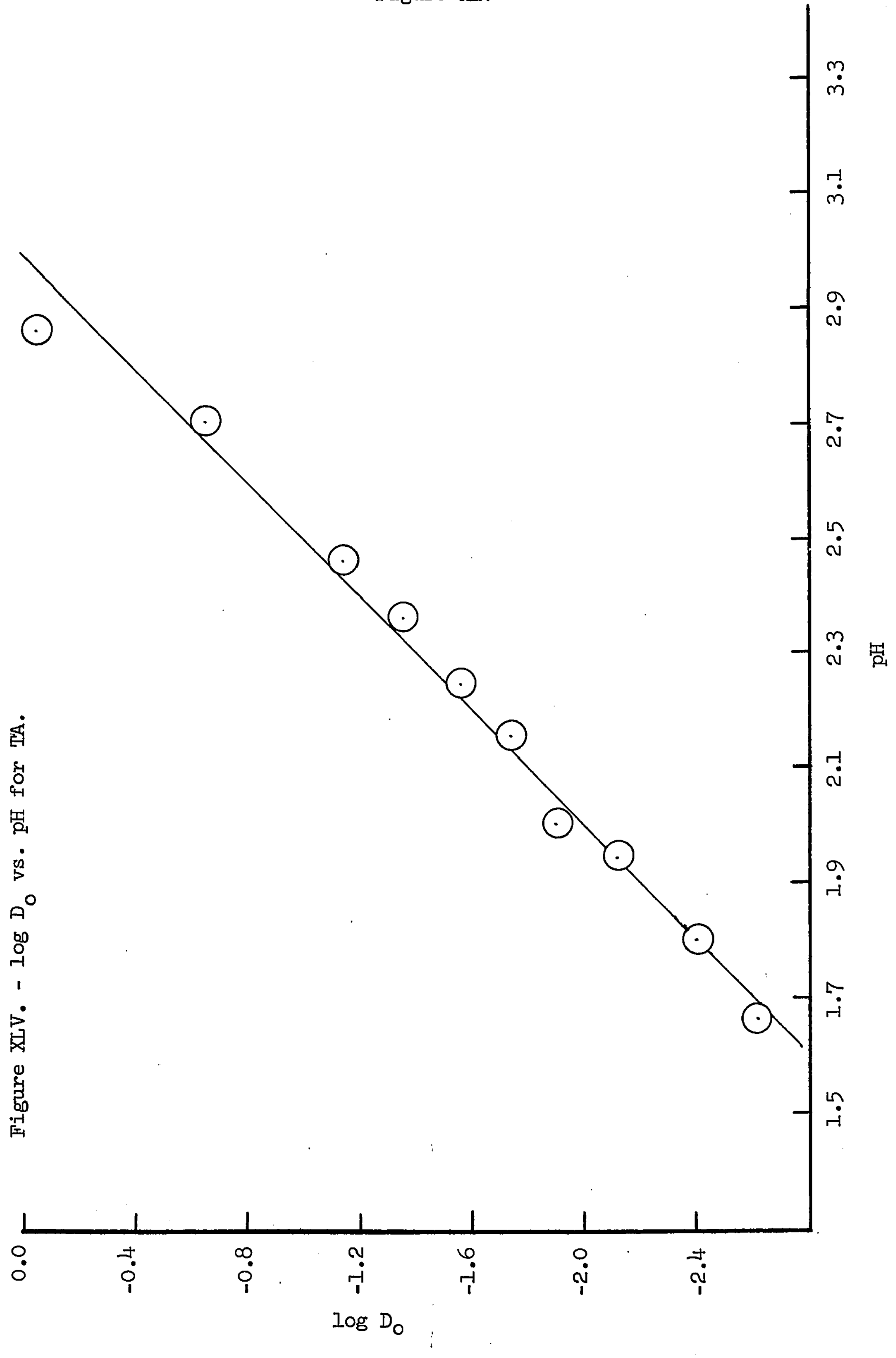

Figure XLV. - log D_o vs. pH for TA.

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Figure XLVI

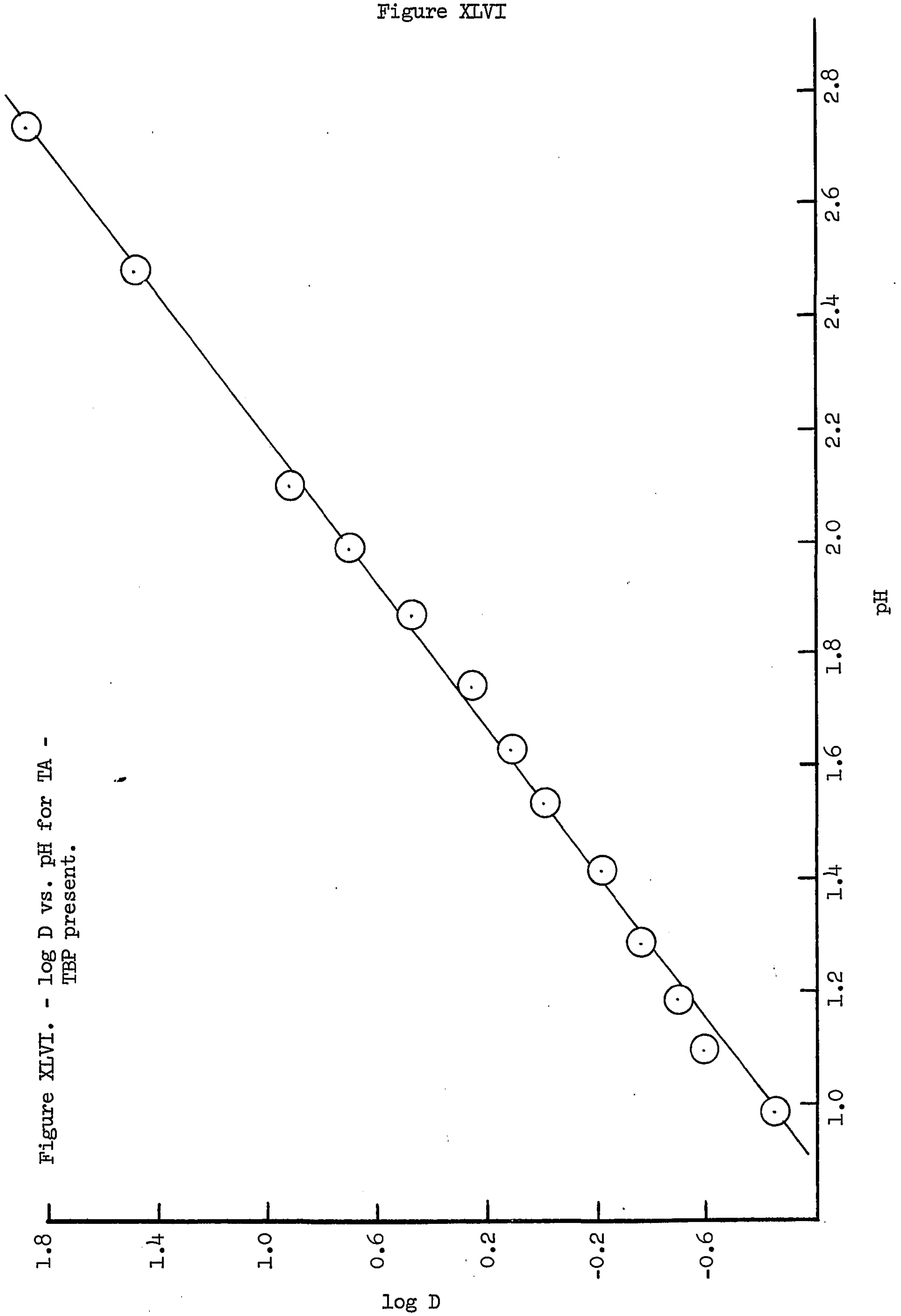

Figure XLVI. - log D vs. pH for TA - TBP present.

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Figure XLVII

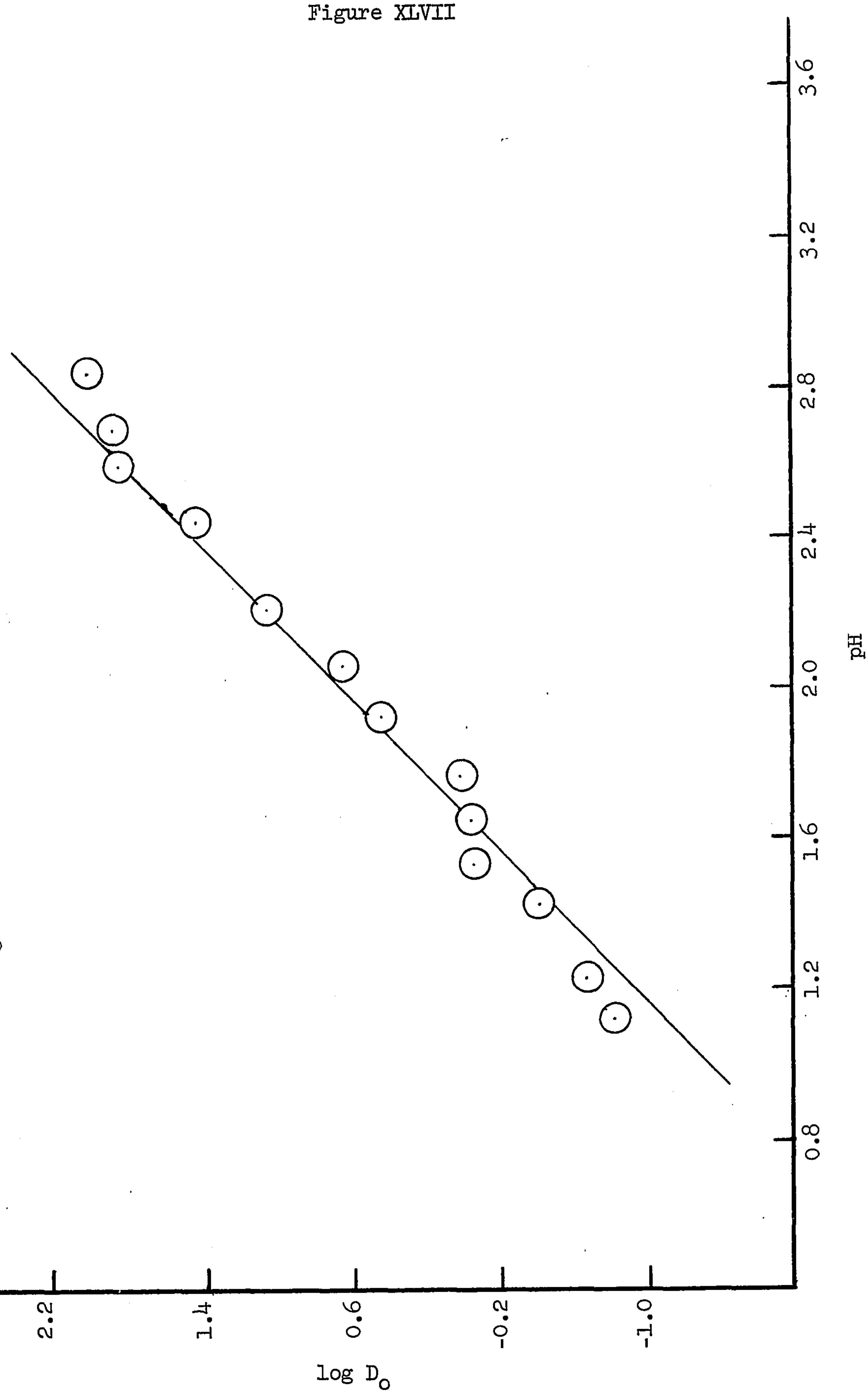

Figure XLVII. - log D_o vs. pH for TTA.

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Figure XLVIII

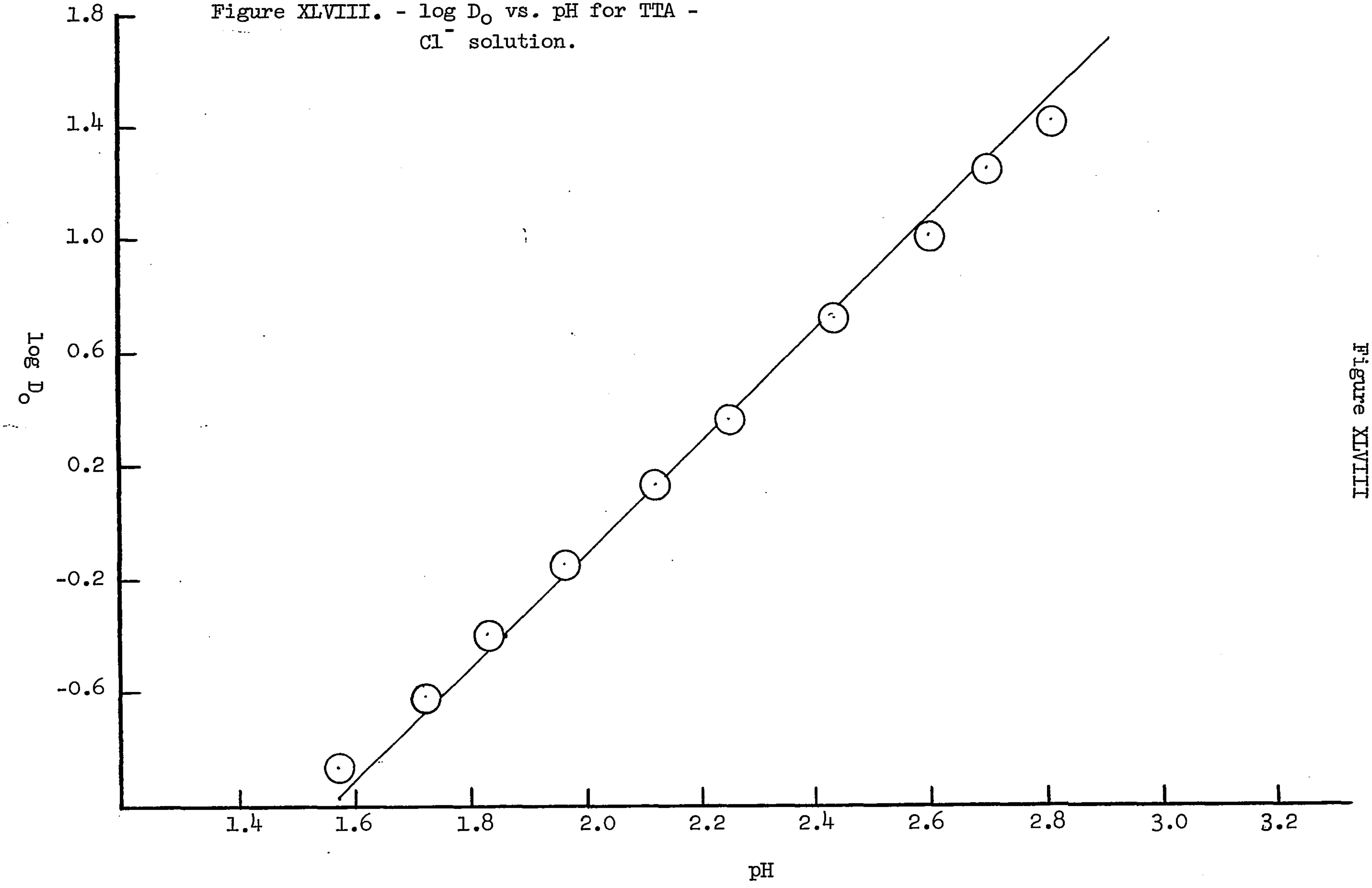

Figure XLVIII. - log D_o vs. pH for TTA - Cl^- solution.

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Figure XLIX

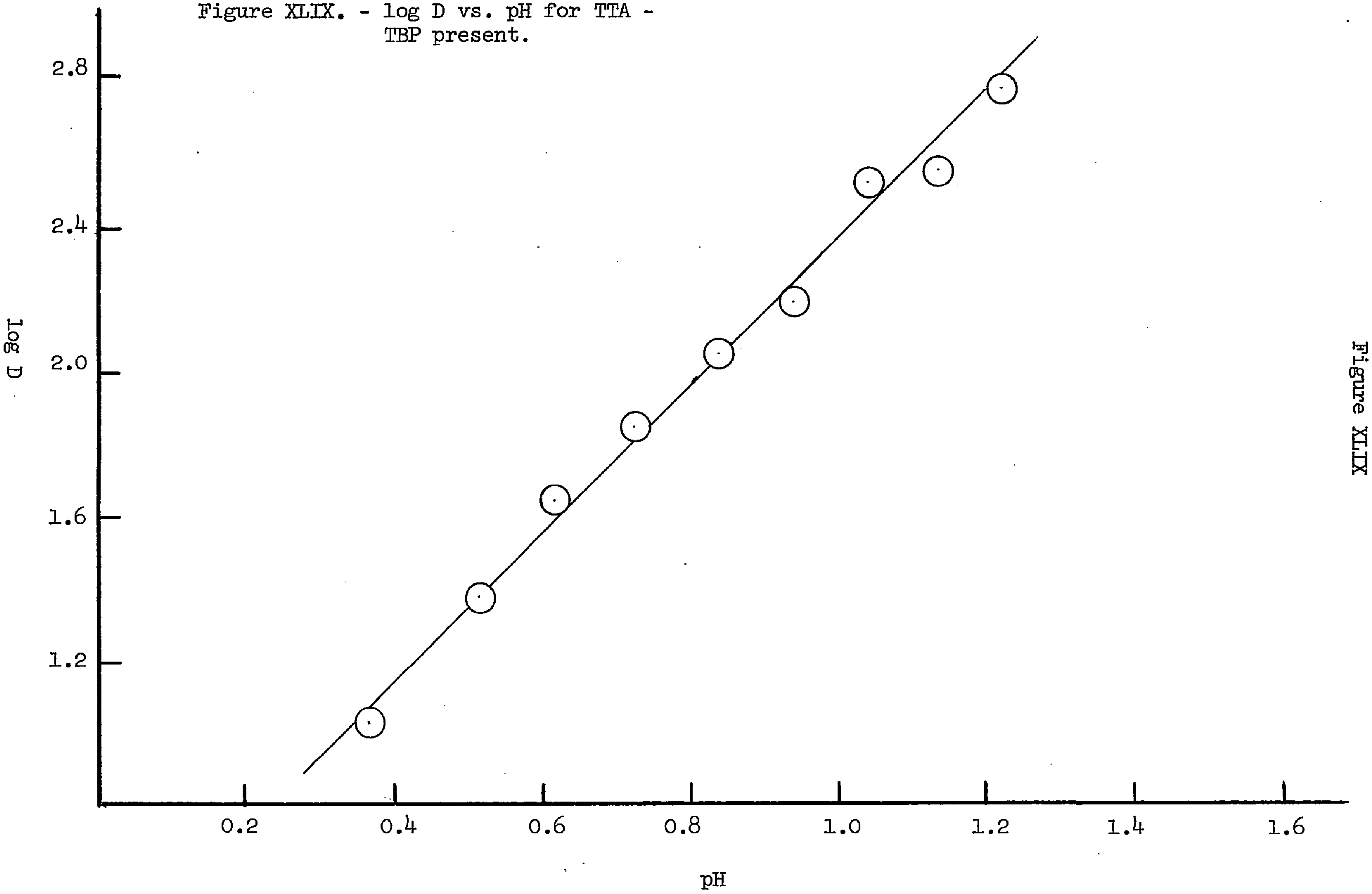

Figure XLIX. - log D vs. pH for TTA - TBP present.

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Figure L

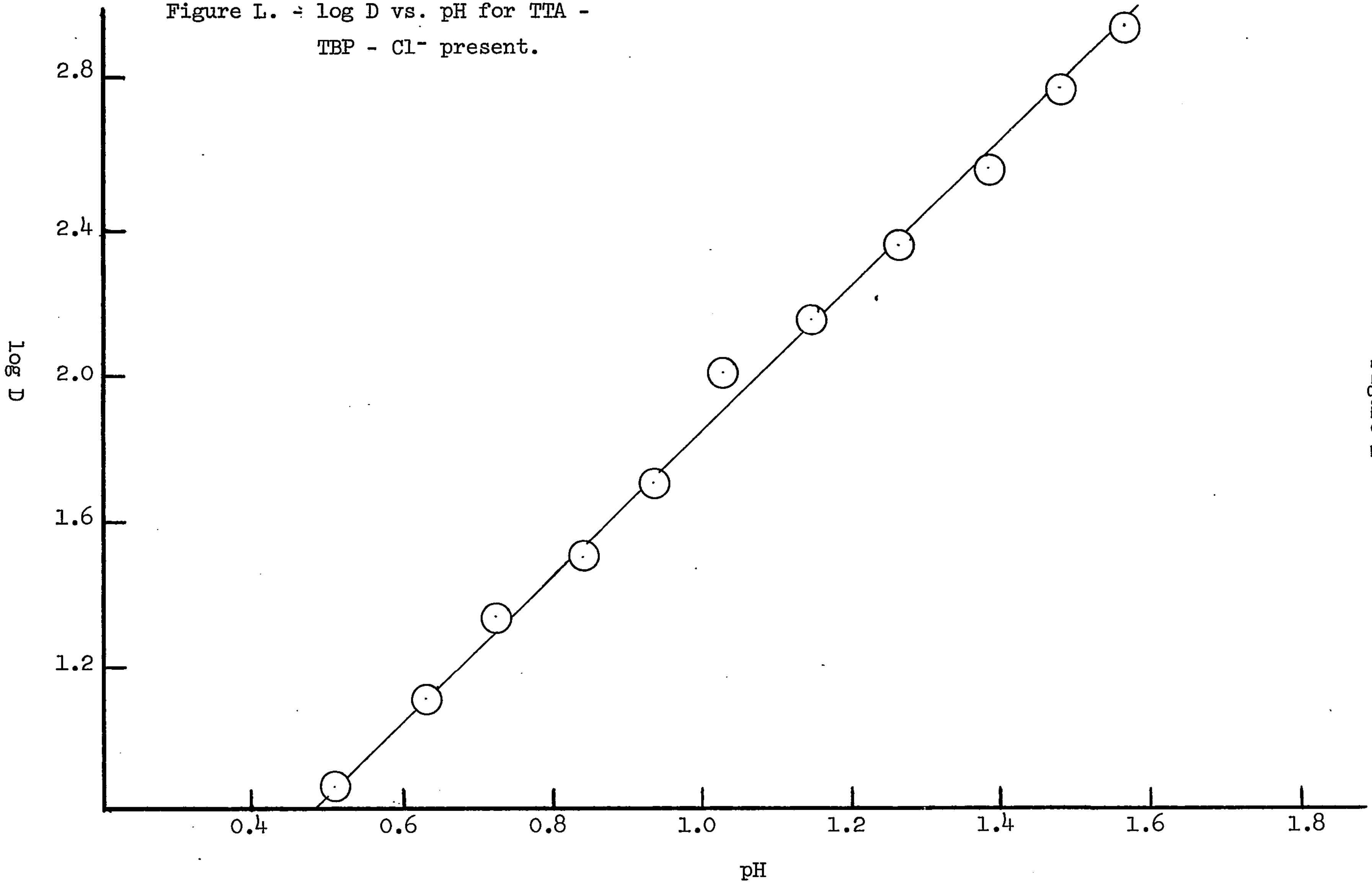

Figure L. - log D vs. pH for TTA - TBP - Cl^- present.

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Figure LI

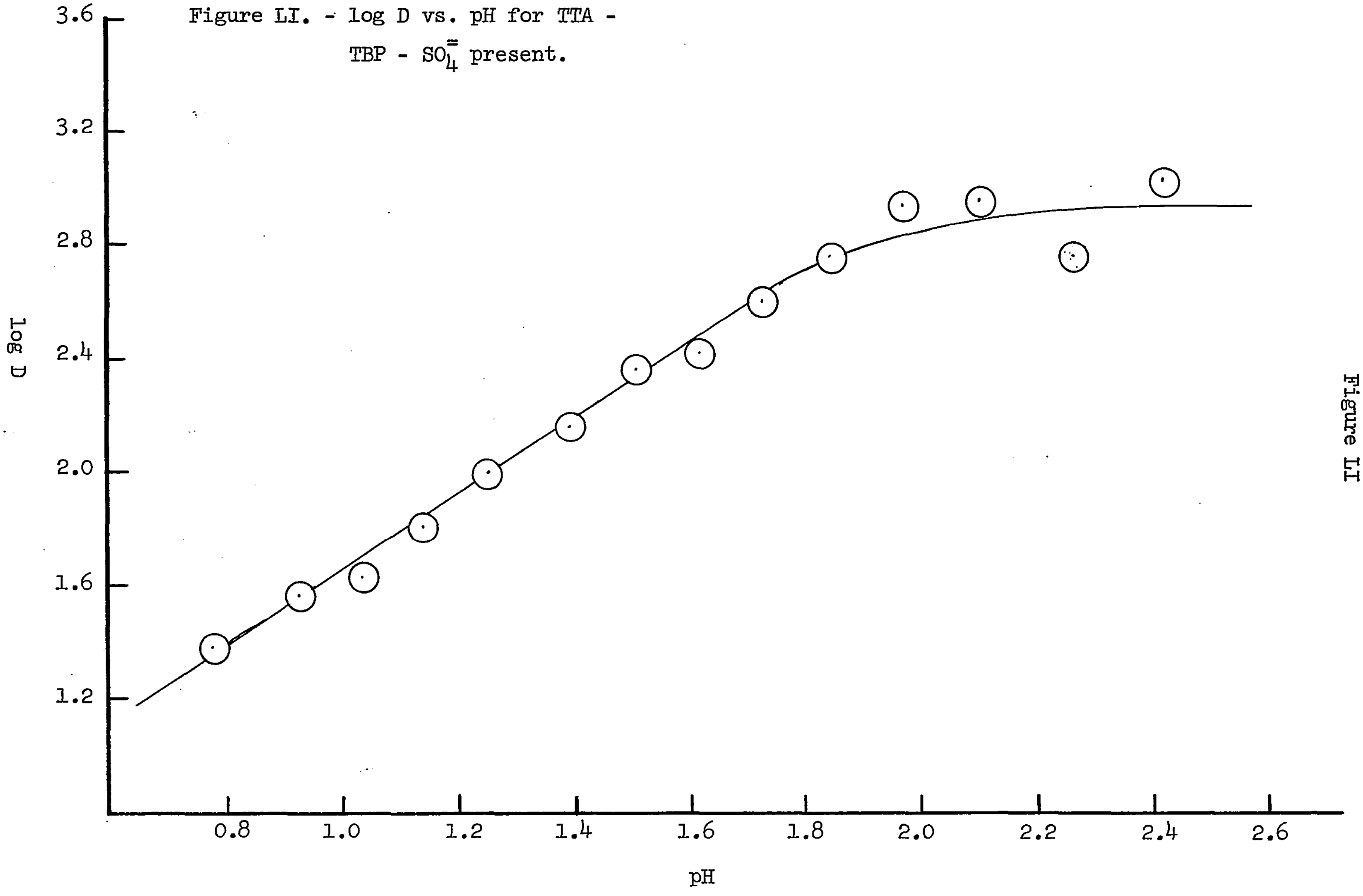

Figure LI. - log D vs. pH for TTA - TBP - $SO_4^=$ present.

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