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Controlled-Potential Polarography In Liquid Ammonia: Inorganic Half-Wavepotentials

Ronald Alan Head
University of the Pacific

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CONTROLLED-POTENTIAL POLAROGRAPHY IN LIQUID AMMONIA: INORGANIC HALF-WAVE POTENTIALS

A Dissertation
Presented to
the Faculty of the Department of Chemistry
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Ronald Alan Head
May 1964

This dissertation is approved for recommendation to the Graduate Council.

Department Chairman or Dean:

Emerson G. Cobb

Dissertation Committee:

Herschel Frye, Chairman

Howard K. Zimmerman

Milton E. Fuller

Donald K. Wedegaertner

C. E. Wulfman

Dated May 8, 1964

PREFACE

The literature of polarography is so vast that any new publication in the field is likely to have an impact comparable to that of a raindrop falling on an ocean. If, however, through some alchemy of the imagination, the raindrop be transformed to quicksilver and accompanied by discharge of "lightning"; and the "ocean" be a solution under carefully controlled conditions, then the effect may be measurable--even reproducible--and thus subject to rational interpretation. Since Jaroslav Heyrovsky's pioneer work in the early nineteen twenties, many such drops have fallen, bringing the science and art of polarography to its present highly developed state. Though superseded by gas chromatography in current popularity and publication rate in this country, polarography has many devoted followers and an almost inexhaustible and growing literature. Within the field, frontiers now being explored include alternating current polarography, oscillographic polarography, derivative polarography, controlled potential polarography, and non-aqueous systems. The present work is in the latter two categories.

At this point, the author wishes to express gratitude and sincere appreciation for many direct contributions of time, service, and equipment by Dr. Herschel Frye ("Blue Leader"), and the following members and former members of "Team A": Dr. Jack Hileman, Dr. Gordon Julian, Mr. James

Larsen, Mr. Anthony Trujillo, and Mr. Gordon Williams. Also deserving thanks is Mr. Clifford Dean, for willing help on several occasions.

Further recognition must go to Dr. Emerson Cobb, who was responsible for initiating this doctoral program and for arranging financial support from the National Science Foundation.

Completion of this work would have been impossible without the help and understanding of my wife, Dorothy, who deserves utmost appreciation for her continuing moral support and dedication to the cause.

Stockton, California R.A. Head
May 2, 1964

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SYMBOLS AND ABBREVIATIONS

A.C.	alternating current
ASTM	American Society for Testing Materials
D.C.	direct current
D.M.E.	dropping mercury electrode
E^{o}	standard reduction potential
$E_{\frac{1}{4}}$	quarter-wave potential
$E_{\frac{1}{2}}$	half-wave potential
$E_{\frac{3}{4}}$	three-quarter-wave potential
F	Faraday, electrochemical equivalent, 96,487 coulombs.
i_d	diffusion current
i_r	residual current
ua	microamperes
n	number of electrons gained, per ion, on reduction
S.C.E.	saturated calomel electrode
TBAI	tetrabutylammonium iodide
TEAB	tetraethylammonium bromide
TEAC	tetraethylammonium chloride
TEAI	tetraethylammonium iodide
TEAP	tetraethylammonium perchlorate
TEPNI	triethyl-n-propylammonium iodide
TMAI	tetramethylammonium iodide
v	volts

PART I

APPROACH

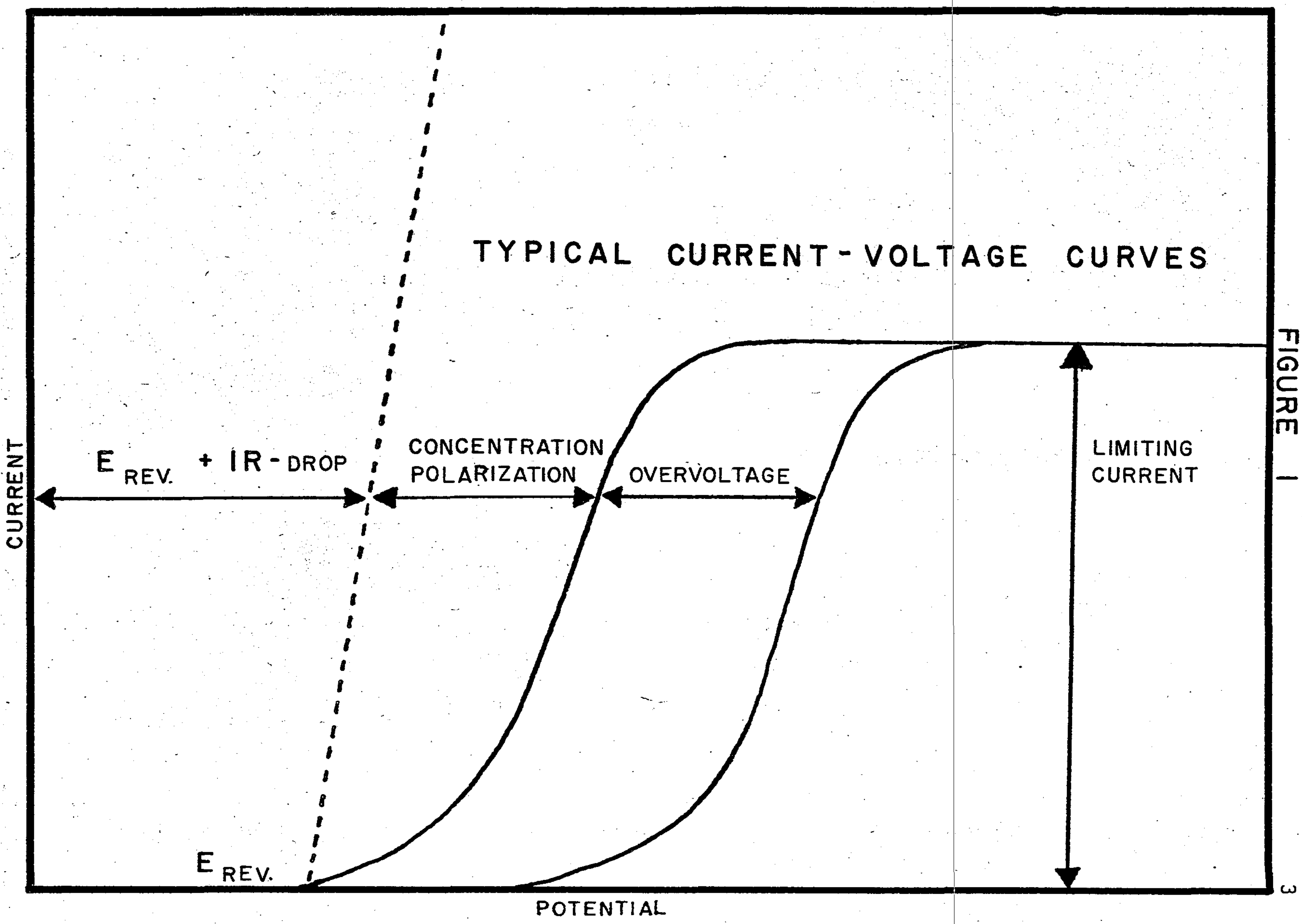
CHAPTER I

INTRODUCTION

Polarography is an electroanalytical technique capable of extreme sensitivity in both qualitative and quantitative applications. Often, however, this sensitivity may be achieved only under highly specific experimental conditions which limit the comparison of results. In its classical form, the method consists of the measurement of current as the electrical potential is gradually increased at a dropping mercury electrode in a dilute solution of one or more reducible substances. The theory of current-voltage relationships in an electrolytic cell is a general foundation of polarography. As the applied voltage is increased in a typical electrolytic solution (Figure 1), no current flows until the reversible cell potential, E_{rev}, is reached. If the electrode reactions are completely reversible, a further increase in voltage would produce a sharp current rise. (line a) At any point along this line, the potential is the sum of the reversible cell potential plus the voltage equivalent to the product of current times cell resistance. The latter voltage is known as the "IR-drop". However, an actual cell will develop opposing voltages which limit the current as in curve b. These opposing voltages are caused by an increase or decrease of ion concentrations near the electrodes.

Concentration gradients, thus produced, require additional applied voltage to match the opposing potential. This condition is called concentration polarization. Furthermore, if a reaction is to take place at an electrode, a certain activation energy, called overvoltage, must be supplied. This is illustrated by the potential increase between curves b and c in Figure 1. The current eventually becomes independent of the applied potential and reaches a limiting value which is governed by concentration, diffusion, and migration of ions.

A typical polarographic wave (Figure 2) resembles the current-voltage curve c in the preceding Figure, except that a small residual current (largely due to capacitance between the electrode drop and its surrounding ion layers) precedes the reduction current rise, and the limiting current is determined by diffusion. If the migration current of reducible ions in the electrical field surrounding the drop can be eliminated by a relatively large concentration of non-reducible ions (the supporting electrolyte), then the limiting current is due solely to diffusion of reducible ions to the electrode surface, and is proportional to the concentration of such ions in the bulk of the solution. This condition makes possible the quantitative determination of many reducible species. Also to be noted in Figure 2 are the regular current fluctuations due to growth and fall of successive



TYPICAL CURRENT-VOLTAGE CURVES

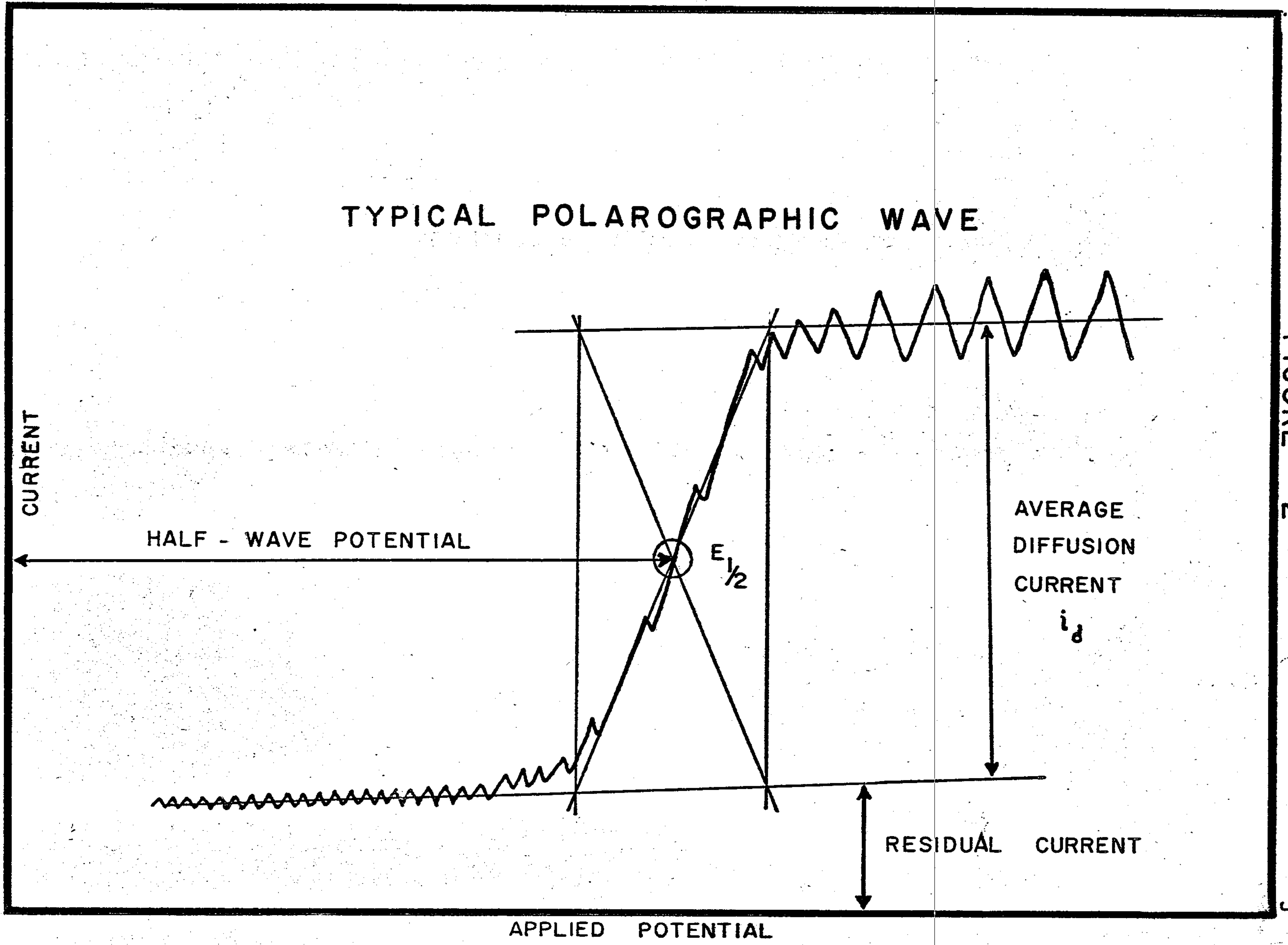
FIGURE 1

mercury drops at the capillary tip, and the important theoretical quantity known as the half-wave potential. This value is uniquely characteristic of a reducible species under certain conditions, and constitutes the basis for qualitative polarography.

The mathematical foundations were established by Ilkovic (1934), and Heyrovsky and Ilkovic (1935). The first of these references gives the derivation of the expression, known as the Ilkovic equation, for the average diffusion current:

$$\bar{i}_d = 607nD^{1/2}Cm^{2/3}t^{1/6} \quad , \qquad (1)$$

where $\bar{i}_d$ is the average diffusion current in microamperes, 607 is a collection of constants and conversion factors at twenty-five degrees centigrade, n is the number of Faradays of electricity required per mole of reducible substance, D is the diffusion coefficient in square centimeters per second, C is the concentration in millimoles per liter, m is the weight of mercury falling from the capillary in milligrams per second, and t is the time interval between drops, in seconds. This equation was the result of considerations involving the interactions of drop-area growth with time, the conical diffusion of spherical ions toward the growing spherical drop, the instantaneous flux of the diffusing ions in the volume increment adjacent to the drop, and electrical equivalent



TYPICAL POLAROGRAPHIC WAVE

FIGURE 2

of ions reduced. Many objections have been made with regard to some of the assumptions in the derivation, but the above equation is in good agreement with experimental results for drop times greater than about two and a half seconds. Faster drop intervals apparently introduce enough stirring to upset the convection-free conditions necessary for proper diffusion. The direct relationship of concentration to current establishes a theoretical basis for quantitative polarography.

The second reference (page 4) gives the theoretical relationships for the fundamental equation of qualitative polarography. For a rapid, reversible reduction at the dropping mercury electrode when the product is soluble in mercury and forms an amalgam at the surface of the drop, the potential of the electrode is given by a Nernst equation of the form

$$E_{d.m.e.} = E_s^o - \frac{RT}{n\mathcal{F}} \ln \frac{C_a^o f_a}{a_{Hg} C_s^o f_s} . \qquad (2)$$

Here, E_s^o is the standard potential of the half-reaction at the dropping electrode, R is the gas constant, 8.3143 volt-coulombs; Tis the absolute temperature, n is the number of electrical equivalents, $\mathcal{F}$ is the electrical equivalent or Faraday, 96,487 coulombs; C_s^o and C_a^o are the molar concentrations of dissolved ion and of the metal in the amalgam--

both at the surface of the drop--f_s and f_a are the corresponding activity coefficients, and a_{Hg} is the activity of mercury in the amalgam. The latter value is practically identical to that of pure mercury and for very dilute amalgams it may be regarded as unity.

The current, i, is proportional to the difference in concentrations of the metal ion in the bulk of the solution and at the electrode surface:

$$i = k_s(C_s - C_s^o). \qquad (3)$$

At potentials corresponding to the diffusion current, i_d, the ions are reduced as fast as they reach the drop surface, so that C_s^o approaches zero, and

$$i_d = k_s C_s \, , \qquad (4)$$

representing a great simplification of the Ilkovic equation. The concentration of metal in the amalgam is also proportional to the current:

$$i = k_a C_a^o \, . \qquad (5)$$

When the above assumptions and relationships are applied to equation (2), then

$$E_{d.m.e.} = E_s^o - \frac{RT}{n\mathcal{F}} \ln \frac{f_a \, k_s}{f_s \, k_a} - \frac{RT}{n\mathcal{F}} \ln \frac{i}{i_d - i} \, . \qquad (6)$$

At the half-wave potential, where $i = {}^{i}d/_{2}$, the last term in (6) becomes zero, so that

$$E_{d.m.e.} = E_{\frac{1}{2}} = E_{s}^{o} - \frac{RT}{n\mathcal{F}} \ln \frac{f_a \, k_s}{f_s \, k_a} \quad . \qquad (7)$$

Substituting (7) in (6) gives the result

$$E_{d.m.e.} = E_{\frac{1}{2}} - \frac{RT}{n\mathcal{F}} \ln \frac{i}{i_d - i} \quad . \qquad (8)$$

This important relationship of the half-wave potential offers a criterion for reversibility of a reaction (assumed in the above derivation) since it predicts a straight line when $E_{d.m.e.}$ is plotted against $\log \frac{i}{i_d - i}$. The slope should be $\frac{2.303\ RT}{n}$ or $\frac{0.0591}{n}$ volts at twenty-five degrees centigrade. The corresponding value at minus thirty-six degrees centigrade would be $\frac{0.047}{n}$ volts. An equivalent criterion of reversibility credited to Tomeš (1937) is more convenient to employ with recorded polarograms where the voltage can be read directly:

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = \frac{RT}{n\mathcal{F}} \ln \frac{3}{1/3} \quad . \qquad (9)$$

This obviates the need for a log-plot since the required potential values can be measured with the aid of a ruler. A difference of $\frac{0.056}{n}$ volts is predicted for a reversible reaction at twenty-five degrees centigrade, and in liquid ammonia at minus thirty-six degrees centigrade the corresponding value would be $\frac{0.045}{n}$ volts. The most conclusive proof of reversibility, and usually the most difficult to obtain, is a composite anodic-cathodic wave whose oxidation half-wave potential at a dropping amalgam electrode is the same as the reduction half-wave potential at a dropping mercury electrode. Practical experience has shown that the relative degree of reversibility can be predicted rather consistently by the steepness of the reduction wave. Thus, the sharper the current rise, the closer the approach to reversibility, making application of the above criteria necessary only with the steepest waves when electron requirements are known. As shown by equation (7), the significance of reversibility here lies in the direct relationship between the half-wave potential and the standard reduction potential. A series of such standard potential values for redox couples in liquid ammonia would, if known, permit predictions regarding the spontaneity of reactions in the medium. Toward the same end, the standard reduction potentials would permit calculations of free energy changes according to the relationship

$$\Delta G = -n\mathcal{F}E^{0} \, , \qquad (10)$$

where ΔG is the recommended designation for the Gibbsian free-energy change. Table I gives values calculated by Jolly (1956) for some oxidation potentials in liquid ammonia:

TABLE I

OXIDATION POTENTIALS IN LIQUID AMMONIA AT 25°C

Half-reaction	E^o_{acid}	E^o_{basic}
$Li = Li^+ + e^-$	2.34 volts	2.70 volts
$Ba = Ba^{++} + 2e^-$	2.2	
$Ca = Ca^{++} + 2e^-$	2.17	2.83
$Cs = Cs^+ + e^-$	2.08	
$Rb = Rb^+ + e^-$	2.06	
$K = K^+ + e^-$	2.04	2.04
$e^- \cdot NH_3 = e^- + NH_3$	1.95	1.95
$Na = Na^+ + e^-$	1.89	2.02
$Mn = Mn^{++} + 2e^-$	0.56	1.7
$Zn = Zn^{++} + 2e^-$	0.54	1.8
$Cd = Cd^{++} + 2e^-$	0.2	1.4
$Pb = Pb^{++} + 2e^-$	0.28	1.4
$Tl = Tl^+ + e^-$	0.25	1.3
$Ni = Ni^{++} + 2e^-$	0.1	1.3
$Co = Co^{++} + 2e^-$	0.0	
$Fe = Fe^{++} + 2e^-$	0.0	
$\frac{1}{2}H_2 = H^+ + e^-$	-0-	
$Cu = Cu^+ + e^-$	-0.36	1.3
$Cu = Cu^{++} + 2e^-$	-0.40	
$Ag = Ag^+ + e^-$	-0.76	1.0
$I^- = \frac{1}{2}I_{2(s)} + e^-$	-1.26	-1.26

The attractive nature of electrochemical analysis as a research tool stems from the concept of controlled introduction of electrical energy into a system of physical-chemical variables. Of course the difficulty lies in the manipulation of the variables or the conditions so as to obtain results in an uncompromised form. Many times, totally unsuspected factors can confuse the issue, then again, the most laborious precautions may turn out to be completely unnecessary. If such occurrences be accepted as a norm for research then liquid ammonia polarography may be regarded as typical, offering both promise and problems in abundant measure.

A general statement of the present problem may be given in a single word--exploration. The phases of the problem can be listed as (1) feasibility, including temperature control, surveys and tests of solubility, and elimination of possible interferences; (2) procedure development, including refinements of technique and equipment, and (3) acquisition and interpretation of data. Preliminary interest was centered on general characteristics of non-aqueous solvents, the possibility of heretofore unknown trends and relationships among the transition metals, and the verification and extension of recorded data.

Since the alkali metal salts were known to be quite soluble in liquid ammonia, it was decided that a repetition of the work of Laitenin and Nyman (1948) would provide a good check on equipment and technique, and would serve as a launching pad to the transition metals. It should be pointed out that, though accepted in wide usage, phrases such as "the polarography of metals" actually refer to metal ions in solution and imply the solubility of a salt of the metal. This is true of the work on alkali "metals" which were dissolved as halides rather than elemental metals. A further semantic variation may become necessary in the light of findings to be presented in Chapter V.

CHAPTER II

RESUME OF RELATED WORK

I. POLAROGRAPHY IN LIQUID AMMONIA

Liquid ammonia has been investigated as a polarographic solvent by several researchers. Laitenin and Nyman (1948) obtained half-wave potentials for the alkali metal iodides using tetrabutylammonium iodide as a supporting electrolyte and a mercury pool as the anode and reference electrode. Since the usual reference electrodes can not be used at the temperature of liquid ammonia, these authors were forced to show that the potential of the mercury pool in liquid ammonia is not affected by iodide ion, then to relate the pool potential to an aqueous reference ($Pb:Pb^{++}$, 0.1N) at twenty-five degrees centigrade by comparison of the same cation (Na^{+}) in both media at the two different temperatures. This involved the assumption that the reduction potential of the solvated cation is the same in liquid ammonia at minus thirty-six degrees and in water at twenty-five degrees centigrade. In another article(1948) the same authors postulated that the dropping mercury electrode functioned as an "electron electrode" in liquid ammonia at potentials more negative than -2.3 volts versus the mercury pool. They concluded that this final current rise was not due to reduction of the tetraalkylammonium ion as would be expected with aqueous supporting electrolytes, but to the dissolution of electrons from the dropping mercury electrode. The potential -2.3 volts (-2.6 volts <u>versus</u> the saturated calomel electrode), was assumed to be the practical limit for polarography in liquid ammonia. (This has been found to be generally true, but an exception will be discussed in Chapter V.)

Nyman (1949) extended the above investigations to include the half-wave potentials of calcium, strontium, and barium in liquid ammonia, again using the mercury pool as the reference anode. Laitenin and Shoemaker (1950) obtained the following half-wave potentials against a Pb:Pb^{++}(0.1N) reference: Cu^{+}, +0.16v; Cu^{++},-0.21v; Tl^{+}, -0.15v; NH_4^{+}, -1.37v; all of which were reversible except for Cu^{+}. Elroy and Laitenin (1953) used the same reference electrode and reported these half-wave potentials: Pb^{++}, -0.01v; Cd^{++}, -0.45v; Zn^{++} -0.89v; Ni^{++}, -0.79v; Co^{++}, -0.04v; Co^{+++}, -1.1v; Cr^{++}, -0.73; Cr^{+++}, -1.4v; all reversible excepting Co^{+++} and Cr^{+++}, which gave poorly defined waves.

The polarography of bromates and chlorites in liquid ammonia was reported by Curti and Locchi (1956). Aromatic nitro- derivatives in anhydrous ammonia were investigated quantitatively with an oscillopolarograph by Curti, Riganti, Locchi, and Meriggi (1960). Half-wave potentials for Tl^{+}, Pb^{++}, Cu^{+}, Cu^{++}, Cd^{++}, and Zn^{++} in liquid ammonia at twenty-five degrees centigrade and ten atmospheres pressure were reported by Schaap, Conley, and Schmidt (1961). Ammonium iodide was used as the supporting electrolyte, and close agreement was obtained with the values previously reported for minus thirty-six degrees and atmospheric pressure.

Lithium perchlorate forms a tetraammoniate which is liquid at twenty-five degrees centigrade. This medium was investigated as both solvent and supporting electrolyte for Tl^{+}, Cu^{++}, Pb^{++}, Cd^{++}, Ni^{++}, Co^{++}, Cr^{+++}, In^{+++}, Zn^{++}, IO_4^{-}, $CrO_4^{=}$, and BrO_3^{-}; and was reported by Dabkowska (1960) and by Hubicki and Dabkowska (1961). The useful range of this medium was given as -0.2 to -1.7 volts versus the mercury pool. Though it gave well-defined and reproducible current-voltage curves, this solvent has the disadvantage of being corrosive to glass.

II. AQUEOUS TRANSITION METAL COMPLEXES

An exhaustive summary of polarographic efforts in this area would be beyond the scope of this work. Therefore, only a few references of a general nature will be given, followed by brief discussions of some of the more specific, recent, and pertinent reports.

Volume II of Kolthoff and Lingane's Polarography (1952) gives results, in periodic groups, obtained by various investigators. Meites (1955) has compiled a table of half-wave potentials for most of the known metals in various oxidation states in several relatively standardized aqueous supporting electrolytes. Vlcek, and Koryta, in separate chapters of Progress in Polarography, Volume I (Zuman and Kolthoff, editors, 1962), have discussed, respectively, mechanisms of electrode processes and structure of inorganic complexes; and the polarography of complex compounds. Vlcek has also written a chapter, "Polarographic Behavior of Coordination Compounds" in Progress in Inorganic Chemistry (Cotton, editor, 1963). Lingane (1941) has related the half-wave potential, the dissociation constant, and the coordination number of complex metal ions as follows:

$$E_{\frac{1}{2}c} - E_{\frac{1}{2}s} \cong \frac{0.0591}{n} \log K_c - p\,\frac{0.0591}{n} \log C_s \ ,$$

where the subscripts c and s stand, respectively, for the complex and the simple ions, K is the dissociation or instability constant, p is the coordination number, and C is the concentration. Reversibility criteria are also discussed. Similar equations have been derived in Meites' book (1955) and in Volume I of Kolthoff and Lingane's Polarography (1952).

Leach and Terrey (1937) observed fairly good waves for the reduction of scandium (III) in 0.1N KCl and LiCl, the half-wave potential being -1.80 volts versus the saturated calomel electrode. In acid solution, the hydrolysis reaction

$$Sc^{+++} + 3\ H_2O \ = \ Sc(OH)_3 + 3\ H^+$$

caused a slight hydrogen pre-wave, well separated from the scandium wave. Noddack and Bruckl (1937) reported a two-stage reduction of scandium sulfate without supporting electrolyte, and similar results for yttrium (III) and lanthanum (III). This may have been due to the hydrogen pre-wave rather than to a true two-step reduction.

The polarography of zirconium in aqueous media is very difficult to achieve due to its very negative half-wave potential preceded by hydrogen discharge. However, Colichman and Lugewig (1953) used anhydrous methanol containing 0.1M LiCl as a supporting electrolyte and obtained two waves with zirconium sulfate tetrahydrate.

According to Ferrett and Milner (1955), niobium gives two waves in ethylenediaminetetraacetic acid solution, the first of which is reversible.

Several isothiocyanatoammine and related complexes of chromium (III) have been studied by Maki, Shimura, and Tsuchida (1958). Tanaka, Ebata, and Sato (1963) have reduced hexamminechromium (III) at the dropping mercury electrode. No well-defined direct current wave could be obtained in an unbuffered neutral solution, but in acid a well-defined two-step wave corresponding to the reduction

$$Cr(III) = Cr(II) = Cr$$

was observed. The first wave was diffusion-controlled and close to reversible.

Technetium has been investigated independently by Magee (1959) and by Miller, Kelley, and Thomason (1960) with similar results showing the existence of a minus one oxidation state. Its other properties tend to resemble rhenium rather than manganese.

Iron (II) in aqueous solution one molar in ammonia and ammonium chloride gave a well-defined reduction wave having a half-wave potential of -1.48 volts versus the saturated calomel electrode, according to Voriskova (1939).

Maki and co-workers (1958, 1959) have investigated many cobalt (III) complexes, including tetraammines, pentammines, and bis-ethylenediamines. Kolthoff and Khalafalla (1963) have reported that the reversible one-electron reduction of hexamminecobalt (III) chloride is shifted to more positive half-wave potentials by the addition of bromide and iodide.

Nickel has been investigated by Maki, Kida and Tsuchida (1959) using tetracyano- and dithiooxalatonickelate (IV) complexes.

Magee (1962) has applied simple ligand field theoretical considerations to the polarography of the noble metals. In summarizing the difficulties involved, he pointed out, in an address delivered to the Tenth Detroit Anachem Conference that

> Platinum metals are not usually determined by polarography as this technique has several disadvantages. For example, the platinum metals catalyze the reduction of hydrogen ion at the dropping mercury electrode. Also the potentials of the various couples of these metals are high, and reduce the salts to metal in contact with the mercury. Other inherent difficulties are that the electrode reaction is slow, and the half-wave potentials are too close to each other.

These difficulties may sometimes be resolved by selective complex formation. Magee suggested that ligands be chosen on the basis of their field strength (i.e. their ability to split the energy levels of d-orbitals in the metals) according to the spectrochemical series

$$I^- < Br^- < Cl^- < F^- < H_2O < SCN^- < pyr < NH_3 < CN^-.$$

In a mixture of rhodium, palladium, and iridium ions, the addition of thiocyanate will selectively complex the rhodium to give a half-wave potential of -0.64 volt, then pyridine can be added to coordinate with palladium (II), giving a half-wave potential of -0.4 volt. The iridium has a catalytic hydrogen wave at -1.63 volt which is sensitive to concentration. Magee and Douglas (1962) have reported the determination of micro-amounts of platinum metals using oscillographic polarography. Ruthenium, rhodium, and palladium in concentrations down to 5×10^{-5}M were determined in solutions of pyridine, ammonium ion, and cyanide ion. No reduction waves were obtained with osmium and iridium. Willis (1944) had previously reported the irreversible polarographic reduction of hexacyano- and hexathiocyanatorhodate (III) with half-wave potentials of -1.47 volt and -0.394 volt respectively. In another article (1945) he reported the almost reversible one-step reduction of tetraamminepalladium (II) in 1M ammonia, with a half-wave potential of -0.797 volt. No satisfactory waves were obtained for osmium, iridium, or platinum. Seifert and Simek (1959) obtained half-wave potentials for red rhodium chloride in various supporting electrolytes as follows: ammonium monohydrogen phosphate, -0.17 volt; ammonium sulfate, -0.02 volt; ammonium thiocyanate, -0.38 volt; and hydrochloric acid, -0.12 volt. No waves were obtained for the yellow form.

III. CONTROLLED-POTENTIAL POLAROGRAPHY

The use of non-aqueous polarography would have been severely limited without some means of automatic correction for the high IR-drops usually encountered. Controlled-potential polarography, pioneered by Kelley, Jones, and Fisher (1959, 1960) is now almost the method <u>sine qua non</u> for high resistance media. An operational amplifier is used as a potential-control amplifier, so that it continuously controls electronically the potential of the polarized electrode with respect to the reference electrode and forces it to equal the applied control voltage, independently of the solution and electrode resistances. The original circuit was quite complicated, with several expensive components. Arthur and coworkers (1961) offered a simpler modification of the above principle, plotting current as a function of the effective voltage, rather than the applied voltage. The required three electrodes were aligned horizontally with the dropping mercury cathode in the center. Arthur and Vanderkam (1961), elaborating on the same idea, stated:

> Although the apparatus was designed originally with only IR-compensation in mind, it also permits the use of electrolysis reference electrodes different from that employed for the stable reference electrode, yet yielding polarograms which are referred to the stable reference electrode alone. Whether the potential of the electrolysis reference electrode is stable or drifting is immaterial.

A compensation error less than ± five millivolts was claimed over the range ± twenty volts.

Probably the least expensive and most convenient way to convert from classical to controlled-potential polarography is to use a circuit similar to that suggested by Annino and Hagler (1963). This circuit (Figure 3, page 25) has been adopted for the present study in liquid ammonia.

Schaap and McKinney (1964) offered the following equation to correct the half-wave potential for uncompensated resistances:

$$E_{\frac{1}{2}} = E_{\frac{1}{2},\text{observed}} + \left(\frac{i_d}{2} - i_{r\frac{1}{2}} \right) R$$

where $i_{r\frac{1}{2}}$ is the average residual current at the half-wave potential, and the other symbols have their customary meanings.

CHAPTER III

EQUIPMENT AND MATERIALS

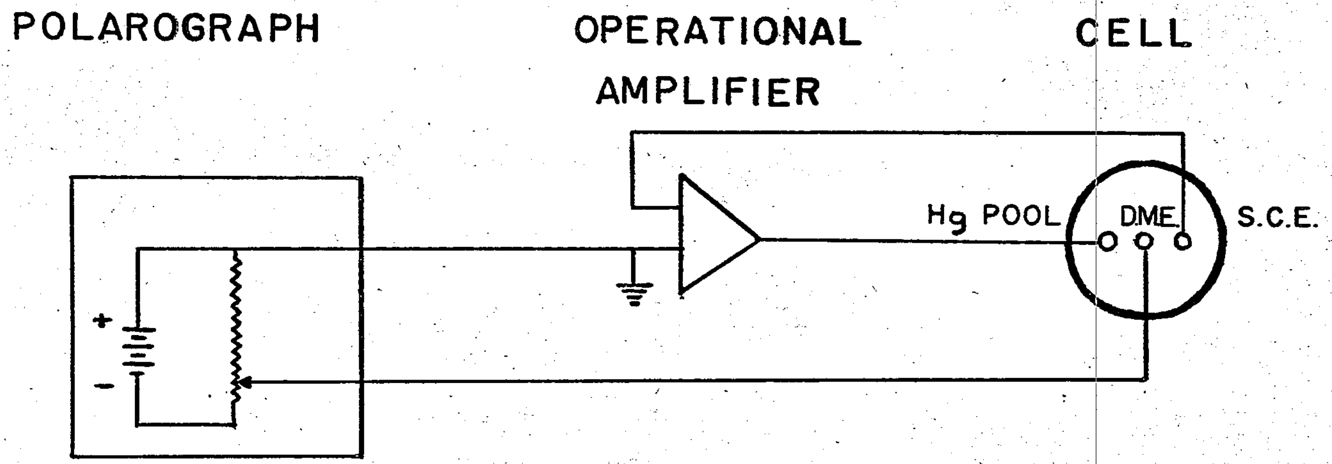
I. INSTRUMENTATION

The instrument used to obtain most of the data in this investigation was the Leeds and Northrup Electrochemograph, Type E. Cited for its simple, rugged design by Meites (1955), this polarograph incorporates a very sensitive microammeter recorder which utilizes the continuous null-balance principle. This insures freedom from errors due to variations in amplifier gain. Four degrees of damping are available, of which the zero (undamped) and the first (galvanometer equivalent) settings were used whenever possible to minimize recorder lag. However, the effects of this lag can be eliminated completely even with higher degrees of damping, since a reverse polarization feature enables one to average the ascending and descending half-wave potentials.

Other control features include an internal standardization against a Weston-type cadmium cell, and a very precise applied potential from plus one volt to minus three volts in three overlapping ranges of two volts each. An automatic polarizer gradually increases (or decreases, if a reverse wave is desired) the potential at a rate of 0.2 volt per minute. The chart speed is fixed at two inches per minute. Also, a current range selector gives eleven convenient choices, from one microampere to one hundred microamperes at full scale. This feature proved useful in examining the detailed form of low and ill-defined waves and maxima. During the course of this investigation, a new Auto-Scan polarograph (Electrochem Company, Olympia, Washington) was obtained. Though its standardization and voltage range setting were somewhat inconvenient, this inexpensive instrument gave results in very close agreement with the Electrochemograph.

Since most of the liquid ammonia solutions had very high (up to a megohm) resistances, it was found to be highly advantageous to employ the principles of controlled-potential polarography so as to eliminate the calculations and corrections of the excessive IR-drop through the solutions. This approach requires the use of an operational amplifier (as described by Annino and Hagler, 1963) which detects any potential difference between the mercury pool working electrode and the saturated calomel reference electrode, then continuously and automatically compensates for this IR-drop by inverting the detected difference and adding it to the applied potential, so that the nominal registered value is the actual potential supplied to the dropping mercury electrode. This has the effect of eliminating the cell resistance. For this reason, controlled-potential, or three-electrode technique is undoubtedly the method of choice in non-aqueous polarography. (Figure 3) The operational amplifier used for this purpose

FIGURE 3



CIRCUIT FOR CONTROLLED-POTENTIAL POLAROGRAPHY in the present research was the Heathkit Model EUW-19A. Its other uses and capabilities are quite extensive and are discussed at length by Malmstadt, Enke, and Toren (1963). Similar instruments, notably the Philbrick Research Amplifier, have been described and used by various authors. Kelley, Jones, and Fisher (1957, 1959, 1960) deserve much credit for pioneering the adaptation of operational amplifiers from computer applications to polarography. It seems safe to anticipate that most of the better quality of electroanalytical equipment marketed in the future will incorporate some form of operational amplifier for improved performance and versatility. Indeed, so-called "instrument synthesizers" have been described (Underkofler and Shain, 1963; Booman and Holbrook, 1963) which employ the operational amplifier as a key component in duplicating the functions of several separate conventional instruments.

II. ELECTRODES, CAPILLARY, AND CELL

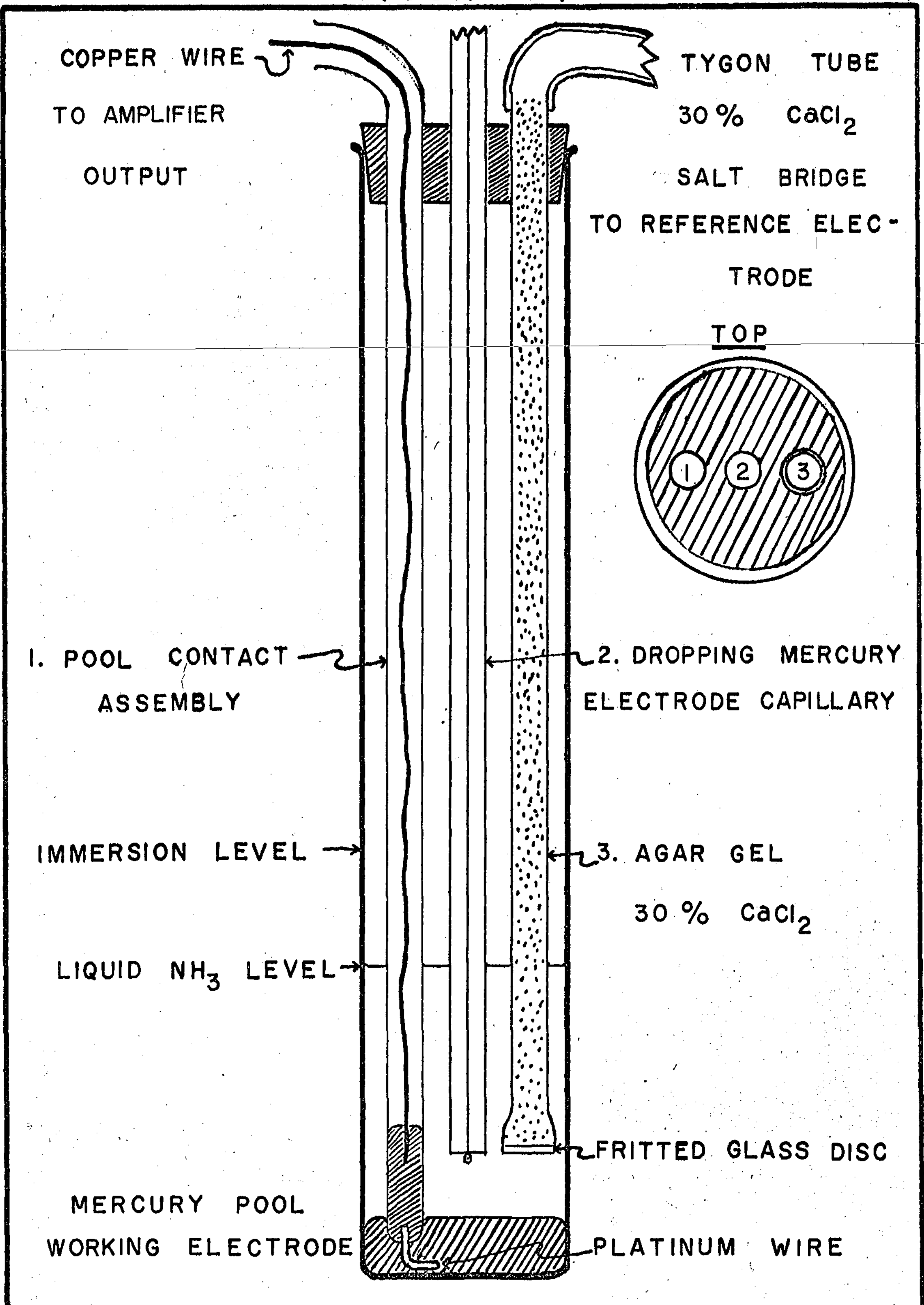
The dropping mercury electrode consisted of a glass reservoir containing triple-distilled mercury, connected by flexible Tygon tubing to a vertical glass tube through a T-joint near the lower end. An eight-inch capillary tube was joined to the vertical mercury column tube by a rigid Teflon fitting. The triple-distilled mercury was eventually replaced with electrolytically purified mercury (Shcherbov and Sagalovich, 1957) with apparently satisfactory results. The commercial "marine barometer" capillary was rated at six to twelve seconds drop time in water, but was found to be somewhat faster in liquid ammonia, depending on the solute, current, and pressure. The capillary constant $m^{2/3}t^{1/6}$ (required in the Ilkovic equation), was found to be 1.132, with m = 0.7500 milligrams per second, and t = 6.6 seconds in saturated tetraethylammonium chloride at minus thirty-three degrees centigrade on open circuit. The constriction near the tip, suggested by Laitenin and Nyman (1948) to avoid clogging by frozen mercury, was not necessary since the ammonia solutions were allowed to come to equilibrium at minus thirty-six degrees centigrade before immersing the capillary tip. The dropping mercury electrode is normally the cathode, and according to the above authors, functions as an "electron electrode" in liquid ammonia. This would mean that, instead of reducing the cation of the supporting electrolyte at its decomposition potential as in aqueous polarography, the electrons simply undergo dissolution in liquid ammonia. This will be discussed further in Chapter V.

For controlled-potential polarography, three electrodes are required. In addition to the dropping mercury cathode described above, a non-polarizable "working" anode, and a reference electrode, usually saturated calomel, were used. Annino and Hagler (1963) used platinum wire for the anode, but it was felt preferable to use the traditional mercury pool so that previous work, without controlled potential, could be repeated and compared. The mercury pool was connected to the amplifier output through an immersed platinum wire, insulated from the ammonia solution by a glass tube. The area of the pool was about six square centimeters, and the mercury was changed with each solution.

For comparison with previous work on metals of Groups I and II, the reference electrode was metallic lead immersed in 0.1N lead nitrate solution. For the remainder of the research on transition and other metals, a saturated calomel reference, thermostatted at twenty-five degrees centigrade, was used. The customary potassium chloride salt bridge, due to its freezing point, could not be used in liquid ammonia. Therefore, a new bridge was devised, consisting of thirty per cent calcium chloride in aqueous solution (freezing point = minus fifty-one degrees centigrade), connected to the reference--and separated from it--by a Pyrex tube having a fritted glass disc on the end and containing about one inch of saturated potassium chloride-agar gel. The other end of the flexible Tygon salt bridge was connected to a similar glass tube immersed in the liquid ammonia solution, where contact was made, without mixing or freezing, by another fritted glass disc with a thirty per cent calcium chloride-agar gel. Normally, some objection might be raised with regard to unknown high liquid junction potentials in a bridge of this type. Potassium chloride is the usual choice for salt bridges because the mobilities of its ions are similar, and liquid junction potentials, though unknown, are kept to a minimum. In the present case, though the calcium chloride bridge undoubtedly has somewhat higher junction potentials, they are compensated for, along with the IR-drop of the cell, by the operational amplifier. The agar gel at the liquid ammonia end of the bridge tended to turn brown with continued use, and was periodically replaced.

A variety of single-compartment polarographic cells was tried. The most convenient of these was a simple heavy-walled Pyrex test tube, having an inside diameter of thirty millimeters, and cut to a length of seven inches. These dimensions provided adequate space for the three electrodes and a convenient immersion depth, both for the electrodes in the cell, and for the cell itself in the cryostat. This home-made cell (Figure 4) was fitted with a three-holed rubber stopper, in which the platinum tipped pool contact fit tightly, and into which the dropping mercury capillary and the salt bridge contact could be easily inserted. An etched mark on the side of the cell designated the approximate thirty milliliter level for rough concentration work.

FIGURE 4



CELL AND ELECTRODE ASSEMBLY

III. TEMPERATURE CONTROL

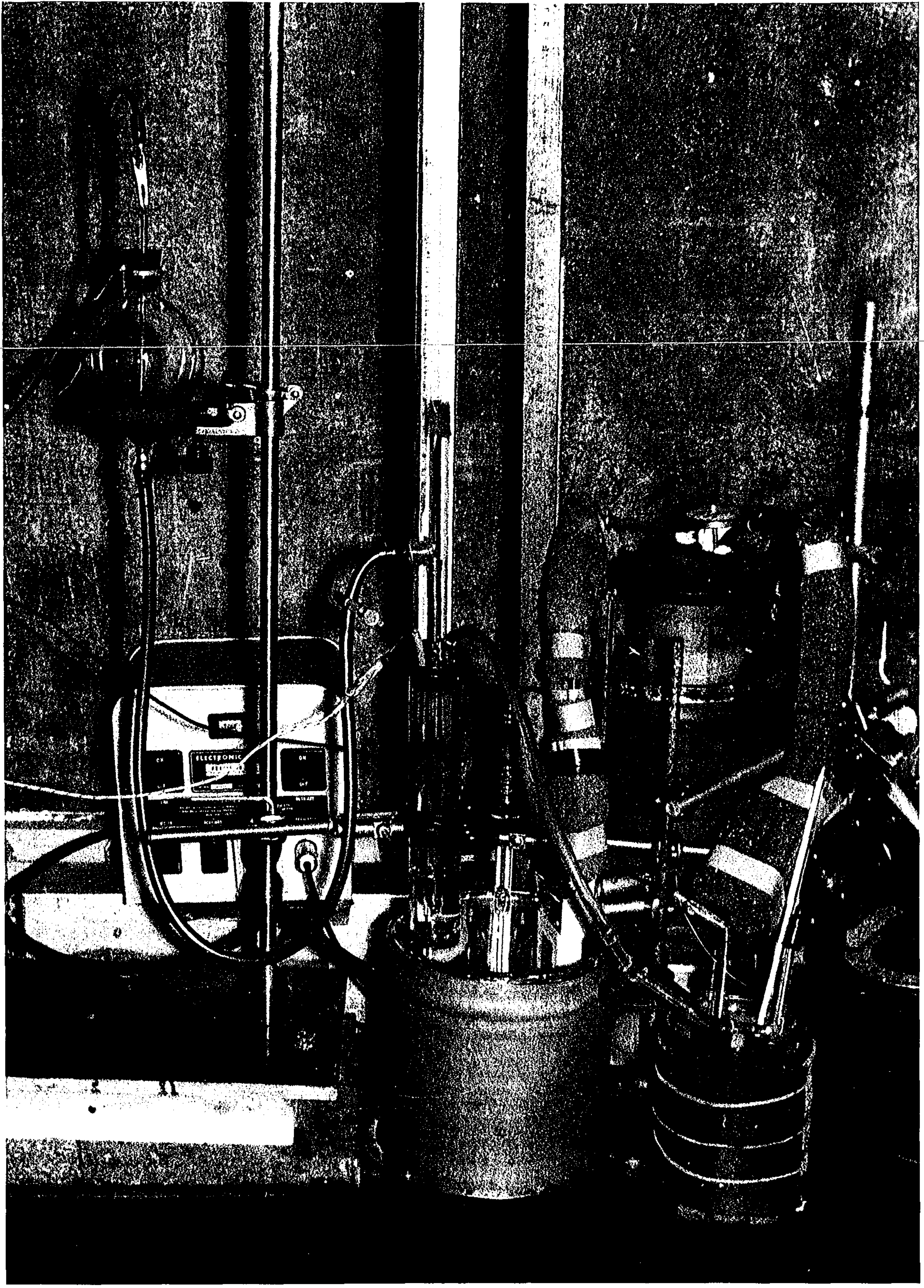
Before this work was initiated, it was pointed out by Frye (1961) that temperature control must be achieved between the limits set by the boiling point of ammonia, $-33.35^{\circ}C$, and the freezing point of mercury, $-38.87^{\circ}C$. A previous attempt at liquid ammonia polarography at this university had failed because of inadequate temperature control. Thus it was recognized that successful completion of the problem would be, to a great extent, temperature dependent. Considerable expenditure of thought and effort were therefore devoted to this phase of the problem and to the associated equipment.

Schaap, Conley, and Schmidt (1961) have described an apparatus for high pressure polarography in liquid ammonia at twenty-five degrees centigrade. Another approach to the problem was used by Vecchi (1953), by Dabkowska (1960), and by Sellers and Leonard (1962), all based on the peculiarity that certain salts are capable of forming ammoniates which are liquid at ambient temperatures. This phenomenon was first reported by Divers (1873) and these liquid ammoniates (notably of ammonium acetate, ammonium nitrate, and ammonium thiocyanate) are known as Divers' solutions. Apparently these and other salts are ammono-deliquescent in a fashion analogous to calcium chloride with water. This approach, loosely classified as "liquid ammonia polarography", obviously involves no serious temperature control problem.

However, for exploratory research, it was felt that a relatively simple, atmospheric pressure cryostat would be the most versatile, as well as the most direct approach. The approach used by Laitenin and Nyman (1948) has been adopted, with notable modifications, for this investigation. Their cold bath consisted of acetone in a large Dewar flask, which also contained a copper cooling coil. A toluene expansion udder served as their regulator, making or breaking contact to start or stop a compressor forcing coolant through the coil. A liquid ammonia solution could be kept at minus thirty-six degrees centigrade by immersing it in this bath. The cryostat for the present investigation (Figure 5) was also maintained at minus thirty-six degrees centigrade, at which temperature the vapor pressure of ammonia is a quite tolerable 665 millimeters. The desired temperature was attained in a magnetically stirred chloroform bath, using a Whirlpool Research Corporation immersion cooler as a heat pump and transfer device. First marketed in the summer of 1963, this cooler employs semiconductors which extract heat by the Peltier effect from the bath and transfer it to a circulating heat sink. A twenty-five ampere 3.8 volt direct current power supply, made by the Whirlpool Corporation, was used to operate the cooler.

Chloroform was chosen as the bath liquid after trying both sixty per cent ethylene glycol in water, and acetone,

FIGURE 5



Cryostat and Accessories

because its low viscosity permitted easier stirring, its low specific heat permitted faster cooling, and condensed water remained immiscible or frozen on the surface where it was easily removed. Covering the bath while not in use kept it clean and minimized the vapor hazard. While carbon tetrachloride would provide the same advantages at lower cost, its vapor is somewhat more toxic.

The heat sink for the cooler was 1-methoxy-2-propanol (Dowanol 33-B), circulated by a silicone-lubricated centrifugal pump through copper coils in another four-liter Dewar flask, which was kept packed with dry ice. The coolant, at minus forty to minus sixty degrees centigrade, circulated through the immersion cooler where probably more cooling was accomplished by conduction than by thermoelectric pumping. Considerable difficulty was experienced with leaks at wired Tygon connections. Acetone caused softening and swelling at room temperature, alternating with shrinking and stiffness at low temperatures. Teflon connectors, threaded into the stainless steel pump housing and sealed with epoxy cement or General Electric RTV-102 silicone adhesive, also leaked. These troubles were eventually eliminated by the use of an all-metal system with Swagelok fittings.

The bath temperature was monitored by an extremely sensitive Precision Scientific Company "Micro-set" differential range mercury thermoregulator. When its expanding mercury contacted a fine tungsten wire in a capillary, it closed a relay (Precision Scientific Company model 62690) which activated both pump and cooler. Starting with bath and heat sink at ambient temperature, about two hours and twenty pounds of dry ice were required to bring the temperature down to minus thirty-six degrees centigrade. During operation, no deviation from this temperature could be detected with an ASTM aniline point thermometer graduated at 0.2 degree intervals.

IV. CHEMICALS

The ammonia was anhydrous refrigeration grade, obtained from Van Waters and Rogers Company. The Interstate Commerce Commission specifications for this grade are: ammonia content not less than 99.95%, and moisture content less than 0.01 milliliter per hundred milliliters of ammonia. (0.01%) Never the less, the gas was passed through a sodium drying tube before being collected. The impurities in anhydrous ammonia consist principally of non-condensable gases (argon, neon, and nitrogen) and traces of oil.

As stated previously, the mercury was either triple-distilled or electrolytically purified according to the method of Shcherbov and Sagalovich (1957).

The tetraalkyl ammonium salts used as supporting electrolytes were Eastman Organic chemicals with the exception of the tetrabutylammonium iodide, which was "Polarographic

Grade" from G. Frederick Smith Company. Lithium perchlorate from G. Frederick Smith was also used as a supporting electrolyte.

Compounds investigated as solutes in liquid ammonia were usually reagent grade, the most notable exceptions being the coordination compounds which were prepared and purified by graduate students working on other research problems. The potassium bromide was Harshaw Chemical Company Infra-Red Quality Reagent.

It should be noted that, in polarographic work, the impurities of greatest concern are (1) those which are reducible at potentials near that of the species being studied, thus masking its reduction wave, (2) those capable of shifting the half-wave potential by forming complexes with the reducible species, and (3) for quantitative work, those capable of suppressing the diffusion current. At the low concentrations of reducible ions employed (10^{-3}M or less), the actual amount of any impurities would be quite small. Furthermore, the effects, if any, of incidental impurities are usually easily recognized. In particular, dissolved oxygen, which must be completely removed and excluded in aqueous polarography, is of little consequence in liquid ammonia, presumably due to extremely low solubility. Moisture, with Group I and II metals, was found to have a pronounced effect on half-wave potentials, therefore anhydrous techniques were required.

With ammine-coordinating transition metals, however, moisture was not a problem because the ammonia not only excludes water, but extracts it from most solutes. This meant that aquo complexes or hydrates of these metals could not be investigated as such, being converted to the corresponding ammines or ammoniates in liquid ammonia.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The following paragraphs will describe operational details associated with a typical "run", including cooling, sample preparation, recording the polarogram, and calculating the half-wave potential.

At the start, all power switches were turned on, so that electronic components could warm up and stabilize while the cryostat was being cooled. These switches, six in number, included (1) the magnetic stirrer, (2) the relay (controlling the power supply to the cooler, and the pump, whose switches always remained on), (3) the polarograph, (4) and (5) the A.C. and D.C. circuits for the operational amplifier, and (6) the vacuum-tube volt meter.

The chloroform bath was cooled to the neighborhood of minus thirty-six degrees centigrade by the direct addition of chipped dry ice, since thermoelectric cooling alone was far too slow. The circulating coolant (i.e. the heat sink for the thermoelectric cooler) was kept between minus twenty and minus thirty degrees centigrade in normal operation by dry ice packed around the copper coils in the large Dewar container. No further attention was necessary during the course of an hour's run, since the regulator and relay automatically turned cooler and pump on and off as required to maintain the desired temperature. Of course, longer runs required periodic replacement of ice for the heat sink.

The polarographic cell, charged with supporting electrolyte and a weighed amount of the compound to be studied, was placed in a dry ice-acetone bath at about minus seventy degrees centigrade. Ammonia gas from the tank was then passed through a sodium-packed drying tube into the cell. After briefly sweeping air from the cell, the delivery tube and stopper were tightened in order to maintain a positive pressure and to speed the condensation. The cell was shaken from time to time in order to aid solution of the sample and supporting electrolyte. After thirty milliliters of ammonia was collected, the tank valve was closed, the delivery tube removed, and the cell and contents transferred to the cryostat. The solute concentration was approximately 10^{-3}M for most of the determinations. About five milliliters of mercury was then added to the cell to serve as a pool for the working electrode. Its addition at this point served also to hasten the attainment of thermal equilibrium between cell contents and bath. The stopper, containing the dropping mercury electrode capillary (with mercury flowing), and the contacts for the working and reference electrodes, was inserted into the cell. At this point, checks were made for vertical alignment, electrode position, and electrical continuity. Before the latter operation, however, it was necessary to balance the operational amplifier--now thoroughly stabilized--at a gain of ten to one, using the likewise stabilized vacuum-tube volt meter. This balance was checked periodically during the recording of polarograms.

The reference cell was placed in its water bath, carefully adjusted to twenty-five degrees centigrade. This temperature was also checked periodically. The polarograph itself was calibrated against its own internal Weston standard cadmium reference cell. Then, with all electrode leads connected, a rapid manual scan of the whole voltage range was made to determine the specific range of interest to be recorded, to determine the lowest possible current range setting (sensitivity) which would keep the whole polarogram on the chart, and to set the degree of damping necessary for the current oscillations of the individual mercury drops. With these settings established, the polarogram was recorded with automatic voltage scanning, both ascending and descending through the pre-determined potential range. After twenty or thirty minutes the recording was repeated in order to verify the constancy of the half-wave potential. Some samples, due to slow solvation or to ligand exchange, exhibited shifting half-wave potentials. In these cases, recordings were repeated at intervals until successive runs indicated that equilibrium had been reached.

On completion of the recordings, all power switches were turned off; the capillary and electrode contacts were removed from the cell and washed thoroughly with distilled water; and the contents of the cell were poured (in the hood) into a beaker where the ammonia was allowed to evaporate and the mercury was recovered. The cell was carefully washed and dried for future use.

The polarograms, carefully labeled as to sample, supporting electrolyte, reference electrode, instrument setting, and date, were removed from the recorder and graphically analyzed for precise half-wave potential values. These values were determined by constructing parallelograms (Figure 2, on page 5) for both ascending and descending waves, whose diagonals intersected at the half-wave potential. These potentials were read to ± one millivolt and averaged for the ascending and descending waves in order to eliminate the effects of recorder lag. This average, due to anomalies in the printed chart paper (Leeds and Northrup Company, Number 626), and the resultant difficulty of maintaining synchronization with the applied potential, was reproducible only to about ± five millivolts. In cases where the diffusion current was poorly defined, reproducibility suffered further from visual error in constructing the parallelograms. The half-wave potentials tabulated in the following chapter are rounded off to 0.01 of a volt, and will usually differ slightly from the corresponding polarogram (Appendix) since only the ascending wave could be included by direct reproduction at the same scale as the chart paper. In most cases, the average half-wave potential is two or three hundredths of a volt more positive than the circled values on the polarograms.

PART II

RESULTS AND INTERPRETATION OF DATA

CHAPTER V

ALKALI METAL COMPOUNDS

I. HALF-WAVE POTENTIALS

Table II, column 1-A, gives the half-wave potentials of alkali metal salts in liquid ammonia as found in the present study. Comparison with previously reported values (column 2-A, Laitenin and Nyman, 1948) shows agreement in the order--that is, more positive with increasing atomic number--but a constant difference of approximately 0.3 volt in magnitude is also apparent. This would seem to indicate internal consistency in the two studies, while the difference is probably attributable to the methods of correcting for IR-drop through the cell. In the earlier study, this correction was made by calculations from (unreported) resistance measurements, while the present work employed automatic compensation by an operational amplifier, amounting to about 0.4 volt with the saturated calomel reference electrode, and 0.02 volt with the lead:lead nitrate reference. Although both studies ostensibly employed the latter reference, the earlier work involved an indirect relationship in which the mercury pool was the primary reference, requiring substitution of sodium half-wave potential values in two different media at two different temperatures, as described on page 13. Measurements in the present work were made directly against the

TABLE II

HALF-WAVE AND REDUCTION POTENTIALS OF ALKALI METALS REFERRED TO THE SATURATED CALOMEL ELECTRODE

A. In Liquid Ammonia

Metal	$E_{\frac{1}{2}}$(Author)	$E_{\frac{1}{2}}$ (L & N)	E^{o} (Jolly)	E^{o} (P & M)
LITHIUM	-2.34 v	-2.04 v	-2.39 v	
SODIUM	-2.00	-1.68	-1.94	-1.98 v
POTASSIUM	-1.94	-1.61	-2.09	-2.12
RUBIDIUM	-1.91	-1.58	-2.11	
CESIUM	-1.83	-1.52	-2.13	

Notes: Column 1 values were measured directly against the Pb:Pb^{++}(0.1N) reference.
Column 2 (Laitenin & Nyman, 1948) related to Pb:Pb^{++}(0.1N) reference by substitution.
Column 3 (1956) calculated from thermodynamic data with H:H^{+} couple at zero.
Column 4 measured against a Hg:Hg^{++} reference by Pleskov and Monosson (1935).

B. In Aqueous Solutions

	$E_{\frac{1}{2}}$ (Z & K)	$E_{\frac{1}{2}}$(Meites)	E^{o}(Latimer)	E^{o} (DeVries)
LITHIUM	-2.31 v	-2.3 v	-2.803 v	-2.7180 v
SODIUM	-2.07	-2.12	-2.472	-2.4717
POTASSIUM	-2.10	-2.14	-2.683	-2.6826
RUBIDIUM	-1.99	-2.03	-2.683	-2.6844
CESIUM	-2.05	-2.09	-2.78	-2.682

Notes: Column 1 and 2 values were measured against the saturated calomel reference.
Column 3 and 4 values are converted from tables based on the normal hydrogen reference electrode.
Initials refer to Zlotowski and Kolthoff (1942). Columns 2, 3, and 4 represent compilations of data from various investigators.

reference cell through a salt bridge whose resistance was included in the compensated cell resistance.

The relatively high value for lithium in both studies is undoubtedly due to its high solvation energy. By tightly coordinating four solvent molecules, lithium ion resists reduction more effectively than the others in its group. (cf. aqueous $E_{\frac{1}{2}}$ and E^{0} values) The less consistent order of the reduction potentials and of the aqueous values in general is not now understood, but may eventually be explainable in terms of interactions among solvation energies, overvoltages, amalgamation energies, hydrogen bonding, and ionic mobilities. In this case, at least, it appears that the polarographic method in liquid ammonia is able to bring out an orderly, fundamental relationship which is masked by extraneous factors in aqueous solutions or by other methods.

From an analytical viewpoint, the ammonia medium offers a slight advantage in that the half-wave potentials are spread over a wider range. In practice, a difference of about 0.2 volt or more is required to give distinguishable waves. While lithium can be distinguished easily in both media, all the other alkali metal waves merge together in aqueous solution. In ammonia it is possible to obtain separate waves for cesium, sodium, and lithium in the absence of potassium and rubidium, as shown in Figure A-6. Similarly, cesium can be distinguished from potassium in the absence of rubidium. (Figure A-7) For the most part, the alkali metals produced reduction waves closely approaching theoretical reversibility, as shown in Table III and its companion Figure 5. The classical criterion of reversibility requires not only that the log-plot be a straight line, but also that its slope agree with the theoretical value; 0.047 in the present case. (see page 8.) In this connection, the abnormal departures of potassium chloride, rubidium bromide, and cesium iodide from theoretical reversibility seems to be associated with lower concentrations (cf. i_d values) where the solvent influence becomes appreciable.

II. THE SOLVENT WAVE

Although ignored by earlier workers in this area, there is a sixth "alkali metal" which must be considered because of its special relationship to the solvent. The ammonium ion (or ammoniated proton), when added as a halide salt and reduced under the same conditions as the alkali metals above, shows a half-wave potential of -1.68 volts with the lead:lead nitrate reference, and -2.13 volts with the saturated calomel reference. This same wave is also obtained without the addition of ammonium salts, indicating a contribution by the medium itself. (Figures A-8, A-9, and A-10)

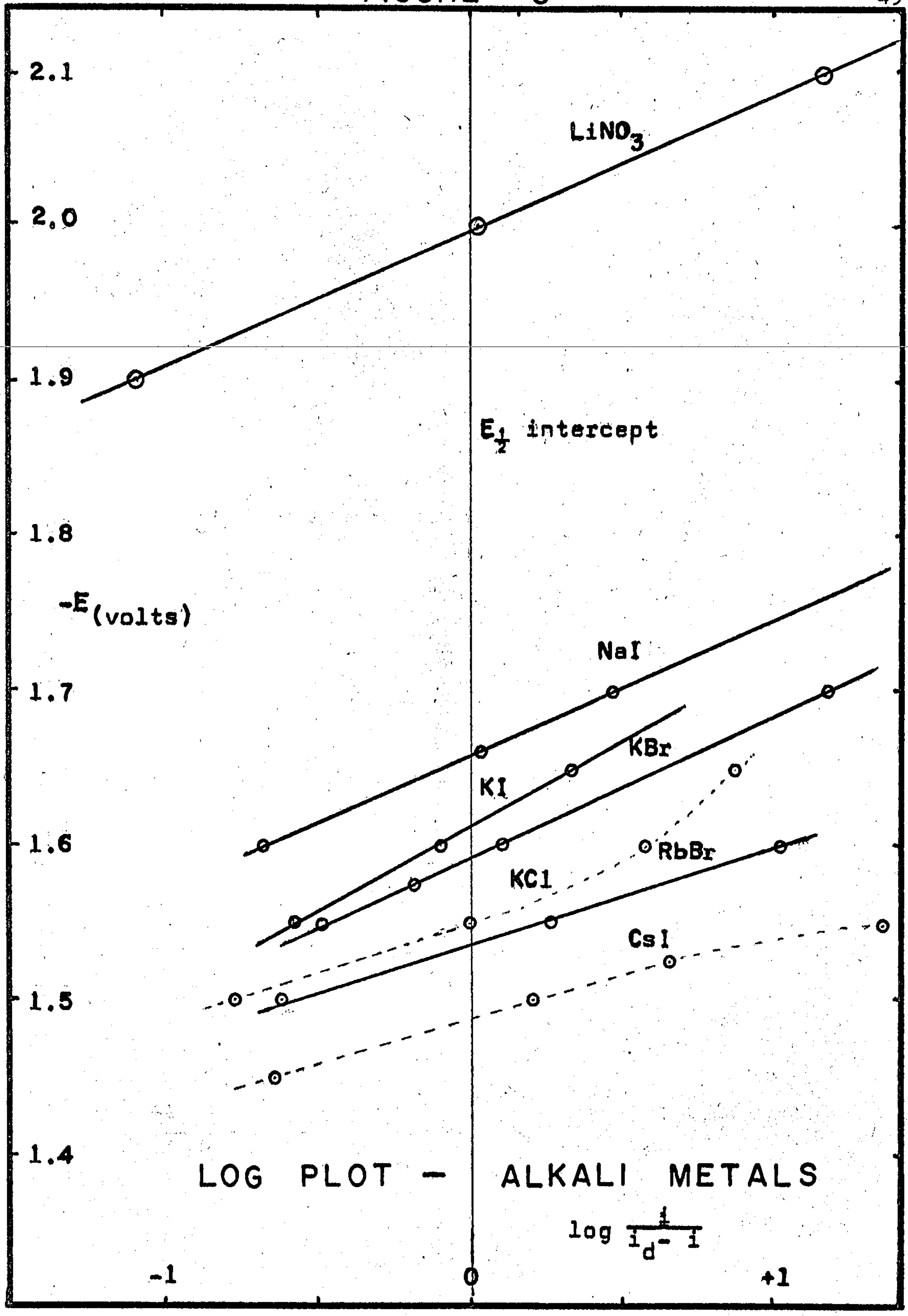
At first it was thought that this recurring wave must be due to contamination; the possibility of moisture and

TABLE III

LOG-PLOT DATA FOR ALKALI METALS

Metal Salt	E volts	i μa	i_d μa	$\frac{i}{i_d - i}$	$\log\frac{i}{i_d - i}$	Slope $m_{rev.}$=0.047
$LiNO_3$	-1.90	3.0	39.0	0.084	-1.076	
	-2.00	20.5		1.08	0.033	0.046
	-2.10	36.5		14.8	1.17	
NaI	-1.66	24.0	43.0	1.12	0.048	
	-1.70	34.0		2.96	0.471	0.046
	-1.80	44.0		44.0	1.643	
NaBr	-1.60	12.0	66.0	0.222	-0.654	
	-1.65	33.0		1.00	0.00	0.045
	-1.70	53.0		4.07	0.610	
NaCl	-1.60	11.0	52.6	0.265	-0.577	
	-1.65	26.0		0.977	-0.009	0.046
	-1.70	43.0		4.46	0.645	
KI	-1.55	12.5	58.0	0.275	-0.561	
	-1.60	26.0		0.813	-0.090	0.057
	-1.65	40.0		2.22	0.346	
KBr	-1.50	2.5	50.0	0.053	-1.279	
	-1.55	12.5		0.324	-0.490	
	-1.575	20.0		0.667	-0.176	0.046
	-1.60	28.0		1.27	0.104	
	-1.70	47.0		15.7	1.20	
KCl	-1.50	1.0	6.80	0.172	-0.765	
	-1.55	3.4		1.00	0.00	(0.06)
	-1.60	4.9		2.58	0.588	(0.08)
	-1.65	6.0		7.50	0.875	(0.18)
RbBr	-1.50	3.4	17.5	0.241	-0.618	
	-1.55	11.3		1.82	0.260	(0.05)
	-1.60	16.0		10.6	1.03	
CsI	-1.45	2.8	14.8	0.233	-0.632	
	-1.50	9.1		1.60	0.203	(0.04)
	-1.55	14.2		23.7	1.38	

FIGURE 6


2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
-E (volts)
LiNO$_3$
$E_{\frac{1}{2}}$ intercept
NaI
KBr
KI
RbBr
KCl
CsI
LOG PLOT — ALKALI METALS
log $\frac{i}{i_d - i}$
-1
0
+1

calcium ion seepage from the agar gel of the salt bridge could not be ignored. However, complete removal of the suspected bridge and scrupulous attention to anhydrous procedure failed to eliminate the wave. The "blank" test solution consisted of thoroughly dried, saturated tetrabutylammonium iodide (G. Frederick Smith Company, Polarographic Grade) in sodium-condensed and redistilled anhydrous ammonia, polarographed against a dry, triple-distilled mercury pool reference, all in a closed, pre-dried glass cell. (Figure A-11) Although the wave was quite small (i_d = 1.2 microamperes) under these conditions, it became larger and more troublesome when other solutes were present. At any rate, it was necessary to exonerate the bridge contact in order that the three-electrode IR-compensation could be used with confidence. Another consideration which reduced suspicion regarding the gel was its distance from the dropping mercury electrode, with the knowledge that diffusion is extremely slow in an unstirred solution at this temperature (minus thirty-six degrees centigrade), and that the migration current was suppressed by the supporting electrolyte.

On the other hand, the concentration of ammonium ion in pure ammonia is very low: 1.7×10^{-15} molar, based on the ionization constant 1.9×10^{-33} at minus fifty degrees centigrade; though not as low as 4.4×10^{-17}, calculated in an earlier report. If this concentration prevailed under polarographic conditions, there should be no possibility of a wave when the lower limit of detection is not less than 10^{-8} molar under the most favorable conditions. However, the observed wave occurred so consistently, regardless of supporting electrolyte or sample, that its origin must be explainable on one or more of the following bases:

1. Shift of solvent ionization equilibrium to produce additional ammonium ion by the removal of NH_2^-, e.g. by formation of insoluble mercuric amide.

2. Enhanced solvent ionization by introduction of moisture from hydrated samples. This is often unavoidable with certain salts and oxidation states of transition metals, unless, of course, air-stable non-aqueous complexes are available, or unless tedious inert atmosphere techniques are employed.

3. Sample-catalyzed ammonium ion reduction. This seems to be the case with simple platinum compounds, from which the metal itself is spontaneously reduced by contact with the dropping mercury at zero applied potential. A slight pre-wave appears just before the usual potential for the wave in question. (Figure A-12) This type of behavior has been frequently reported with aqueous solutions ("water current") and with organic compounds ("catalytic hydrogen wave"), and is discussed in some detail in Chapter XIII of the Kolthoff and Lingane treatise (1952).

4. Potential-induced ionization of ammonia in the electrical double layer surrounding the cathode drop, followed by reduction of the ammonium ion at the drop surface. This may be the process operating in the polarogram for pure liquid ammonia with no supporting electrolyte as shown in Figure A-10. The gradual current rise with constant slope is characteristic of a constant resistance. Notice that the rise occurs at the usual reduction potential for ammonium salts, approximately -2.0 volts <u>versus</u> the saturated calomel reference electrode.

Electrode processes and reaction mechanisms in general are among the more hazardous realms for speculation, but the fourth suggestion above appears to be the most generally applicable, and with the admittedly limited, yet considerable evidence available, the following mechanism seems at least plausible:

1. $2\ NH_3 = NH_4^+ + NH_2^-$ (Induced ionization in the double layer surrounding the drop)
2. $NH_4^+ + e^- = NH_3 + H$ (Cathode reaction)
   $H + Hg = H\ (Hg)$ (Amalgamated or adsorbed)
3. $Hg = Hg^{++} + 2\ e^-$ (Anode reaction)
   $2\ NH_2^- + Hg^{++} = \underline{Hg(NH_2)_2}$

Step 1. above should be facilitated by proton bridging in the cold solvent. The formation of either atomic or molecular hydrogen in step 2 would not be surprising even though no gas bubbles were evident at the low current density used. The overvoltage required for evolution of hydrogen on mercury is even higher in liquid ammonia than in water, according to Pleskov (1939). Furthermore, visible and audible "gassing" was produced in the present work with the dropping mercury electrode in liquid ammonia by increasing the current to forty milliamperes from an auxiliary power supply. With regard to step 3, the originally shiny mercury pool anode was frequently observed to have a white film covering the surface after repeated runs with the same sample. Although it was not separated and analyzed, the film could have been mercuric amide from the pure solvent, or mercuric amidohalide when halide supporting electrolytes were used.

It should be emphasized that the solvent wave (ammonium ion or catalytic hydrogen reduction) described above was quite distinct from the "electron dissolution" reported by Laitenin and Nyman (1948) and verified in the present study. The relationship between the two phenomena can be seen in Figure A-13, with the usual 0.5 volt separation including a current decrease between the ammonium ion half-wave potential and the final current rise due to electron dissolution. The latter event normally constitutes the negative potential limit for polarography in this medium, while the ammonium wave is a complicating factor which may distort other reductions in the near vicinity of potential. (Cf. potassium chloride, pages 47f.) The negative limit may be extended, however, by adjusting the ammonium ion concentration to a value sufficient to prevent the usual sharp current rise due to direct electron dissolution. For example, in a 10^{-3} molar solution of ammonium chloride, with no other supporting electrolyte, there was a gradual current rise beginning at about -2.0 volts <u>versus</u> the saturated calomel reference (ammonium ion reduction), which leveled off at -2.6 volts (i_d = 8 microamperes) and there was <u>no further current rise</u> as the potential was increased to -3.0 volts (Figure A-14).

It has been shown that the lithium wave (Figure A-1) is well-formed, even though it occurs well beyond the potential for ammonium ion reduction. (The extreme depression of current just before the final rise was also obtained by Laitenin and Nyman but no explanation was offered. It seems reasonable, in view of the high solvation energy of lithium ions, to attribute this depression to a temporary depletion of electrons in the bulk of the solution while the solvated lithium ions are being reduced.) If the lithium wave can be obtained following the ammonium wave, it should be possible to obtain waves for even more difficultly reducible cations, including tetraalkylammonium ions, provided that the final current rise can be delayed by sufficient concentration of ammonium ions. This is equivalent to pH adjustment in aqueous solutions, and raises the interesting possibility of a similar logarithmic system for ammonium ion concentration in liquid ammonia, extending theoretically from one to thirty. If the ammonium ion concentration is too large, however, its own reduction will cause the final current rise, beginning at -2.0 volts versus the saturated calomel reference (Figure A-8, III and IV).

It is not known to what extent the ammonium wave influences the half-wave potentials of the alkali metals. Although no separate waves occurred, it would certainly seem that ammonium ion is a contributor to the waves of rubidium, potassium, and sodium. Potassium, whose chemical properties closely match those of ammonium ion, often has a wave with a broken slope (Figures A-16, A-20, A-21, and A-25) at concentrations low enough to be influenced by the solvent wave.

III. ION PAIRS

"All electrolytes exist in ammonia solutions as slightly dissociated ion-pairs. It might be said therefore, that there are no strong electrolytes in liquid ammonia." The first part of this statement by W.L. Jolly (1956) was tested with a series of potassium halides in which it was expected, in the case of ion-pairs, that the larger and more polarizable anions would make reduction of the cation more difficult. And, of course, in the case of complete ionization, the anion should have no effect. The results were as follows:

TABLE IV

ANION INFLUENCE ON HALF-WAVE POTENTIAL

$Pb:Pb^{++}$(0.1N) REFERENCE

Salt	Supporting Electrolyte (1)	$E_{\frac{1}{2}}$ volts	Supporting Electrolyte (2)	$E_{\frac{1}{2}}$ volts
KF	TBAI	-1.66	TEAP	-1.71
KCl	TEAC	-1.53	TEAP	-1.54
KBr	TEAB	-1.56	TEAP	-1.56
KI	TBAI	-1.57	TEAP	-1.58

Note: Polarograms for this table are Figures A-3, and A-15 through A-21.

The first set of supporting electrolytes has anions matching the sample compound (except for KF), while the secone set has the same anion and greater, uniform solubility. This appears to be immaterial; but the consistent variation of half-wave potential with the sample anion is strong evidence for the existence of ion-pairs in liquid ammonia solutions. The exceptional behavior of aqueous fluorides is well-known, but in this case there is good reason to doubt whether the wave represents the reduction of potassium at all, since it closely matches the solvent wave, and the solubility of fluorides is generally low.

Table V (page 57) gives the observed half-wave potentials with several other potassium compounds as measured in ammonia against the Pb:Pb^{++} (0.1N) reference.

TABLE V

HALF-WAVE POTENTIALS: MISCELLANEOUS POTASSIUM COMPOUNDS

Sample	Supporting Electrolyte	$E_{\frac{1}{2}}$ volts	Appendix Figure	Comment
$KMnO_4$	TEAP	No wave		purple solution
KCN	TEAP	-1.65	A-22	solvent wave?
$K_3Fe(CN)_6$	TEAP	-1.65	A-23	sample not completely soluble; solvent? KCN?
K_2CrO_4	TEAP	-1.64	A-24	
KNO_3	TEAP	-1.58	A-25	
KCNS	TEAP	-1.56	A-26	

Since the above values were reproducible to plus or minus five millivolts, the reductions could not be a matter of an independent cation receiving an electron at some specific, invariable potential peculiar to that cation alone. For this reason, liquid ammonia polarography, and polarography in other non-aqueous media of low dielectric constant, should not be expected to yield a single precise half-wave potential for a given cation. The anion too, should be specified as a pertinent variable; its influence in the preceding series extends over a range of approximately 0.1 volt.

The choice of potassium compounds for the study of anion influence was made for the sake of variety, before it was realized that the solvent itself was a contributor in precisely this region. The anion influence might be spread over a wider range by the choice of any test cation other than potassium. Of course the solvent influence could be minimized by using larger concentrations of sample, but the migration current becomes troublesome when the ratio of sample concentration to that of the supporting electrolyte is too high (greater than 1:50, for most aqueous solutions).

IV. SUPPORTING ELECTROLYTES

It should be recognized that the choice of the supporting electrolyte is a major problem in non-aqueous media. The dilemma consists of finding a compound which is sufficiently soluble to suppress the migration current, and which also has a reduction potential high enough to permit a reasonable range of usefulness. In this respect, the tetraalkylammonium halides are superior to alkali metal halides in reduction potential, but inferior in solubility. This was one of the main reasons that no precise quantitative work was undertaken with diffusion currents and concentrations in this study. Such work would also require the re-calibration of volumetric containers at minus thirty-six degrees centigrade. Laitenin and Nyman (1948) determined the concentrations in liquid ammonia of some saturated tetraalkylammonium salts to be as follows: tetramethylammonium iodide, 0.0042M; tetrabutylammonium iodide

0.0057M; and tetraethylammonium iodide, 0.021M. Of these three, the last named is best able to suppress the migration current for quantitative work, but unfortunately it is not available commercially in the same high degree of purity as the G. Frederick Smith tetrabutylammonium iodide. This company now has tetraethylammonium perchlorate, which is soluble to the extent of 0.07M at minus thirty-six degrees centigrade. This appears to be the best choice at present, but as they become available, the following list of ammonia-soluble organometallic compounds should be tested for precise solubility and reduction potential for use as supporting electrolytes:

Organolithium compounds -all
Ethylcalcium iodide
Dimethylgallium chloride -very soluble
Diphenylgermanium dibromide
Tribenzylgermanium iodide
Triphenylgermanium sodium -very soluble
Triethyltin iodide
Tripropyltin iodide
Propyltin triiodide
Dibenzyltin diiodide .

These were selected on the basis of solubility and structure from Lange's Handbook of Chemistry, Ninth Edition (1956).

CHAPTER VI

TRANSITION AND MISCELLANEOUS METAL COMPOUNDS

As a class, the transition metals offered much more difficulty for liquid ammonia polarography than did the alkali metals. The difficulties fell into one or more of the following categories: insolubility, irreducible complex formation, and spontaneous reduction. However, some interesting waves were obtained, as will be seen. Table VI gives a list of qualitative solubilities of various classes of inorganic compounds. Volume VIII (page 200) of Mellor's treatise (1928) also has a long list of qualitative solubility observations for specific compounds in ammonia. Very little quantitative data on ammonia solubilities is available.

With the generalizations from Table VI in mind, the samples chosen for analysis were usually iodides, bromides, thiocyanates, or nitrates. When it appeared that the solubility or reducibility would be favorably affected for a certain metal, some of the available coordination compounds were studied.

It was naturally expected that ammine formation would occur, but the rate and extent of this coordination--sometimes involving displacement of other ligands--was not always known. For the compounds which gave reduction waves, runs were repeated at intervals until a constant half-wave potent-

TABLE VI

SOLUBILITIES OF CLASSES OF INORGANIC COMPOUNDS IN LIQUID AMMONIA

ALKALI AMIDES	Soluble, except for Li and Na salts
ALKALI METALS	Soluble
AMMINE-METAL CATIONS	Soluble. The most highly hydrated cations tend to have the greatest solubility in liquid ammonia.
AMMONIUM SALTS	Soluble, except for salts of insoluble oxy-anions below. NH_4NO_3, NH_4CNS, and NH_4OAc are ammono-deliquescent.
ARSENATES	Insoluble
CARBONATES	Insoluble
CYANIDES	Soluble
HALIDES	Soluble, increasing with atomic number. Exceptions: most fluorides, $ZnCl_2$, and $CaCl_2 \cdot 2H_2O$.
NITRATES AND NITRITES	Soluble
OXIDES AND HYDROXIDES	Insoluble
PERCHLORATES	Soluble
PERSULFATES	Soluble
PHOSPHATES	Insoluble
SULFATES AND SULFITES	Insoluble, except for $(NH_4)_2SO_4 \cdot 3\ NH_3$.
SULFIDES	Insoluble
THIOCYANATES	Soluble

ial was obtained. Table VII presents the half-wave potential values of seventeen metallic compounds in periodic order of vertical family groups. Unfortunately, and for various reasons, none of these groups is completely represented here.

Scandium chloride gave no wave at all in tetraalkylammonium halide supporting electrolytes, but in tetraethylammonium perchlorate a double wave was obtained, the first step of which was reversible. Maxima were present at both steps. No yttrium compounds were tested. Three separate attempts with lanthanum nitrate were unsuccessful. In tetraethylammonium perchlorate, a gradual current rise spanning 0.6 volt was the only result. (To regress before proceeding further, it should be mentioned that the alkaline earth metals were purposely omitted from the study, inasmuch as they had already been reported in liquid ammonia by Nyman in 1949. However, the wave obtained with calcium chloride is included because of its role in the salt bridge. Figure A-27 appears to be practically indistinguishable from the solvent wave.)

From Groups IV-B and V-B, none of the compounds tested appeared soluble, with the exception of bis-[2,4-pentanediono]oxovanadium IV, which gave a blue-green solution. No acceptable waves were obtained in these groups.

Chromium proved to be noteworthy for two reasons. First, it is the only element in its vicinity of the periodic table known to form a variety of stable coordination com-

TABLE VII

HALF-WAVE POTENTIALS vs. THE SATURATED CALOMEL ELECTRODE OF TRANSITION AND OTHER METAL COMPOUNDS IN LIQUID AMMONIA

Sample Compound	Supporting Electrolyte	Half-Wave Potentials 1st Wave	2nd Wave	Appendix Figure
$ScCl_3$	TEAP	-1.99 v	-2.18 v	A-28
~~$Cr(en)_3(SCN)_3$~~	~~TEAP~~	~~-1.50~~	~~-1.8~~	~~A-29~~
$Cr(en)_2(SCN)_2$ SCN	TEAP	-1.73	-1.93	A-30
$Cr(C_2H_3O_2)_3$	TEAB	-1.80	-2.07	A-31
$Co(NH_3)_6\ (NO_3)_3$	TEAP	-0.86		A-33
$RhCl_3$	TEAC		-1.83	A-34
RhI_3	TEAB	-1.28	-1.84	A-35, 35a
$Pd(NH_3)_2(NO_2)_2$	TEAB	-1.22		A-36
CuBr	TEAB	-0.90		A-38
$Cu(SCN)_2$	TEAB	-0.92		A-39
AgCN	TEAB	-0.79		A-40
AgCN	TEAB, KCN	-2.03		A-40a
$Zn(CN)_2$	TEPNI	-1.81		A-41
CdI_2	TEAB	-1.31		A-42
$In(ClO_4)_2$	TBAI	-1.5		
$TlNO_3$	TBAI	-0.60		A-43
$Tl(ClO_4)_3$	TEAB	-0.61		A-44
$PbCl_2$	TEAB	-0.80		A-45

pounds with nitrogen donor atoms. (Molybdenum and tungsten, in the same family, may share this distinction to a much less degree: $MoO_3 \cdot 3\ NH_3$ is recorded by Mellor's Volume VIII, in which the bromides and chlorides of Mo (III), Mo (V), W (V), and W (VI) are also noted as giving red solutions in liquid ammonia.) According to Sanderson (1960), all the neighbors of chromium preferentially coordinate with oxygen rather than nitrogen donors. The second reason for the interest in chromium is that it gives a double reduction wave in aqueous solution, corresponding to

$$\text{Cr (III)} \xrightarrow{e^-} \text{Cr (II)} \xrightarrow{2e^-} \text{Cr (0)}.$$

Whereas the first step is reported to be reversible in aqueous acid solutions (Tanaka, Ebata, and Sato, 1963), it was the second step which met reversibility criteria in liquid ammonia solutions of chromium (III) complexes. Of the many chromium (III) compounds tested, it appears that ammine, halide, and oxygen complexes are usually insoluble in liquid ammonia, while ethylenediamine and thiocyanate ligands give yellow-orange solutions with this cation. Chromium (III) acetate was exceptional not only in its solubility, but also in having a second wave whose slope corresponded to a reversible <u>one</u>-electron reduction:

$$\text{Cr (III)} \xrightarrow{2e^-} \text{Cr (I)} \xrightarrow{e^-} \text{Cr (0)}.$$

It should be emphasized that wave slopes, log-plots, three-quarter- and one-quarter-wave potential differences, and similar data can not simultaneously be used as confirmation for both reversibility and electron requirements. The reduction steps proposed here are to this extent speculative, pending verification of electron involvement by independent methods.

No maxima appeared in the chromium (III) waves, but the suggestion of a pre-wave may signify that adsorption occurs before the first reduction wave. (Brdicka, 1942) The height of the second wave should be the same as that of the first, assuming that a stoichiometric amount of the intermediate oxidation state is the only contributor. The additional height observed for the second wave (Figures A-30, A-31) is further evidence of solvent participation. This enhanced second wave occurs also in aqueous solutions, and was attributed by Lingane and Pecsok (1949) to protolytic ionization or hydrolysis of the aquo complex:

$$Cr(H_2O)_6^{+++} = Cr(OH)(H_2O)_5^{++} + H^+ .$$

The proton, diffusing faster than the chromium complex, is responsible for the increased current. The analogous behavior in liquid ammonia seems likely.

Rapid hydrolysis in air, with loss of chlorine, prevented the successful solution and polarographic reduction of molybdenum (V) and tungsten (VI) chlorides. Their waves should prove interesting, but will require inert atmosphere techniques in the sample preparation.

No waves were obtained for elements of Group VII-B, owing to a lack of soluble compounds.

No true reduction waves were obtained from the iron, ruthenium, and osmium compounds which were tried. Peculiar behavior was noted for both iron (II) and (III) compounds in that they produced a marked depression of the current (Figure A-32).

Hexamminecobalt (III) nitrate gave an orange solution having very low interfacial tension with mercury, as evidenced by the exceedingly rapid drop rate. It produced only a single wave, whereas ammoniacal aqueous solutions give two waves for this compound (Figure A-33).

Rhodium (III) received considerable attention because it was the only noble metal whose ammine complex was not reduced spontaneously by contact with mercury at zero applied potential. Anhydrous rhodium (III) iodide was reduced in two steps, both of which appeared to be preceded by catalytic reduction of hydrogen. The red crystalline form was used exclusively, and it produced solution colors ranging from pink to orange. The hydrated chloride samples had a definite tendency to shift to more positive half-wave potentials with elapsed time. The anhydrous iodide, and the chloride trihydrate when dried overnight at 110°C, had perfectly stable half-wave potentials, but only a single wave could be obtained for the dried chloride. This wave, in tetraethylammonium chloride, matched the second wave of rhodium (III) iodide in tetraethylammonium perchlorate. The slopes of the two iodide waves appear to be close to reversible if the reduction occurs as

$$\text{Rh (III)} \xrightarrow{2e^-} \text{Rh (I)} \xrightarrow{e^-} \text{Rh (0)} .$$

Iridium (III) chloride and iodide appeared to be insoluble in ammonia, and gave only solvent waves. Spontaneous reduction should occur with simple iridium compound solutions.

Nickel (II) chloride formed an insoluble violet ammine complex. The polarogram showed only the solvent wave. Palladium (II) chloride and bromide likewise yielded only solvent waves, but dinitrodiamminepalladium (II) gave a well-formed reduction wave (Figure A-36). Platinum (II) bromide appeared to undergo spontaneous reduction, giving only the catalytic hydrogen and solvent wave (Figure A-12). Platinum (IV) iodide gave a yellow solution (I^-?) and a catalytic wave which merged with the usual solvent wave.

In Group I-B, it should be noted that practically the same half-wave potential was obtained for copper (I) and (II), possibly indicating that the initial one-electron reduction of copper (II) is either spontaneous or takes place at a potential too positive to show a wave at the dropping mercury electrode. However, Kolthoff and Lingane (1952) have observed that the standard reduction potentials of copper ions in aqueous solutions favor spontaneous disproportionation of copper (I) to give copper (II) and metallic copper. If this occurs in liquid ammonia, as seems likely, then the observed wave is that of complete reduction of copper (II) in both cases (Figures A-38, A-39).

The formation of soluble, non-aqueous coordination compounds in water solution (e.g. $Cu(NH_3)_4^{++}$) usually results in a shift to more negative half-wave potentials for the metal ion involved. This principle can be used to advantage with noble metals, whose salts are normally reduced spontaneously at the dropping mercury electrode. In liquid ammonia solutions, a complexing agent is required whose ligand field strength exceeds that of ammonia itself. Of the common ligands, OH^-, NO_2^-, and CN^- meet this requirement. In Table VII, silver (I) is seen to undergo a rather drastic shift of half-wave potential (from -0.79 volt to -2.03 volts <u>versus</u> the saturated calomel electrode) when potassium cyanide is added to the supporting electrolyte (Figures A-40, A-40a).

No waves were expected or observed with gold (I) and (III) iodides.

Zinc (II) chloride was insoluble in ammonia, but the cyanide in triethyl-n-propylammonium iodide gave a poorly-formed, irreversible wave (Figure A-41).

Cadmium (II) iodide, in tetraethylammonium bromide, gave a well-formed wave with a slight rounded maximum; the half-wave potential was -1.31 volt (Figure A-42).

Only compounds of the last three metals of Group III-A were tested. Gallium (III) perchlorate-6-hydrate gave only a solvent wave. Indium (II) perchlorate-11-hydrate gave an ill-shaped highly irreversible wave in tetrabutylammonium iodide, the half-wave potential being -1.5 volt. A high maximum occurred on the ascending wave, but not on the descending one. Thallium (I) nitrate in tetrabutylammonium iodide, and thallium (III) perchlorate in tetraethylammonium bromide, gave practically the same half-wave potential. Judging by the shape of the wave in each case (Figures A-43, A-44), it must be that of the lower oxidation state, in contrast to the otherwise similar behavior of copper.

The only other successful reduction was that of lead (II) chloride in tetraethylammonium bromide. The half-wave potential at -0.80 volt was about 0.4 volt more negative than the anodic current rise due to mercury oxidation. The wave was fairly well-formed (Figure A-45).

Table VIII lists all the compounds which were tried, but which failed to give recognizable reduction waves. Visual determination of qualitative solubility was easy with colored

TABLE VIII

COMPOUNDS WHICH DO NOT GIVE REDUCTION WAVES IN AMMONIA *

Antimony III iodide
Barium II chloride
Chromium III chloride
Chromium III nitrate
Chromium VI bromide
Chromyl carbonate
Cobalt II thiocyanate
Cobalt III iodide
   (iodopentammine complex)
Cobalt III chloride
   (dichlorotetrammine complex)
Gallium III perchlorate
Gold I iodide
Gold III iodide
Hafnium IV iodide
Holmium III chloride
Iridium III chloride
Iridium III iodide
Iron II chloride
Iron II iodide
Iron III thiocyanate
Lanthanum III nitrate
Manganese II bromide
Manganese II iodide
Nickel II chloride
Osmium III chloride
Osmium IV chloride
Palladium II chloride
Platinum II bromide
Potassium permanganate
Ruthenium III iodide
Ruthenium III chloride
Scandium III chloride
Silver acetate
Silver iodide
Tantalum V iodide
Tin IV iodide
Titanium IV iodide
Uranyl nitrate
Uranium IV oxalate
Vanadium IV oxide
   (*bis*- 2,4-pentanediono-
   oxo complex)
Zirconyl nitrate
Zirconyl perchlorate

*In tetraalkylammonium halide supporting electrolytes.

compounds and solutions, but for white powders and crystals--often indistinguishable from the supporting electrolyte--the polarogram itself offered the best proof of solubility or of insolubility.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The half-wave potentials of alkali metal compounds were found to be in relative, but not absolute agreement with previously reported values. The constant difference was attributed to the methods employed for IR-drop correction and for relating the applied potential to the reference electrode. The importance of the ammonium ion, a quasi-alkali metal, was emphasized because of its relation to the solvent being studied. A wave, not previously reported, was discovered to originate with the solvent itself, and was shown to be identical with the ammonium wave. The equivalence of this wave to that of proton reduction was noted, and its occurrence at lower (less negative) potentials was observed as a catalytic effect in the presence of certain metals.

Various potassium compounds were studied in order to ascertain the effect of the anion on the half-wave potential of the cation. Variations occurred; regular and predictable variations in the case of the halides; indicating that ion-pairs, rather than free ions, are the diffusing species in liquid ammonia solutions.

Due to a broader spectrum of half-wave potentials, mixtures of alkali metal compounds could be resolved by liquid ammonia polarography in certain combinations which are not feasible in aqueous solution.

Reduction waves were obtained, and half-wave potentials were determined for some eighteen compounds of transition and other metals. The original intention of calculating standard reduction potentials from these half-wave values had to be abandoned because of the scarcity of reversible waves, and because an essential experimental quantity, the concentration of metal in amalgam at the dropping mercury electrode, was not available without great difficulty.

Some forty-one compounds, mainly of transition metals, were found to be either insoluble or spontaneously reduced, thereby failing to give a true reduction wave. It was later realized (and demonstrated in the case of silver) that many compounds in the latter category--mostly noble metals--could have been reduced at more negative potentials had they been converted to cyanide complexes. This must be considered as one of the several promising lines of endeavor to arise from exploration in this general area. Also deserving of further and more intensive work are the relationships among various oxidation states, together with the conditions for their stability. With additional data from comparable oxidation states, it may be that a periodicity of half-wave potentials will emerge from ammonia solution studies. Such a relationship has not been apparent in aqueous electrochemistry.

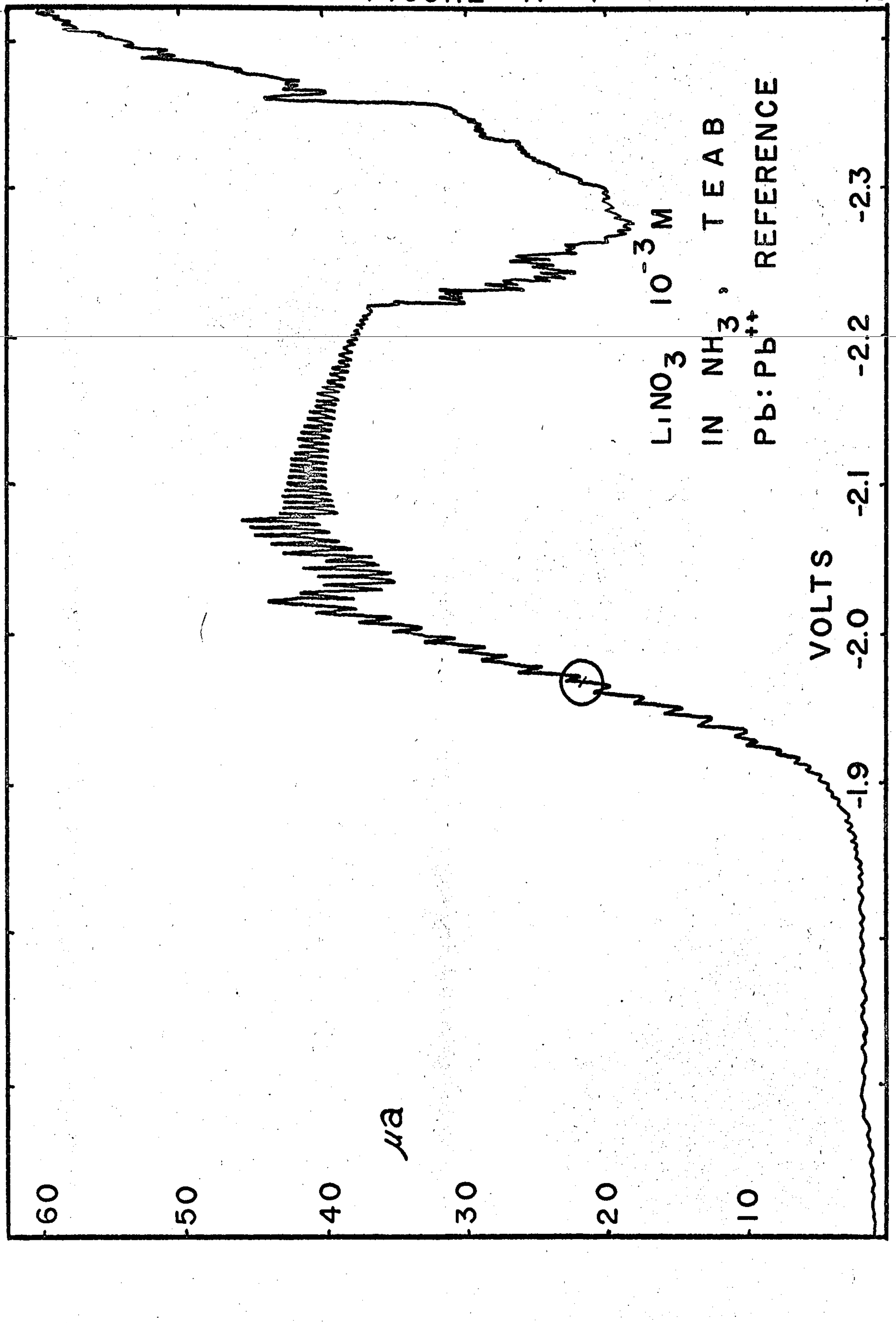
Inert atmosphere techniques would make possible the polarographic testing of compounds, such as tantalum (V) iodide, titanium (IV) iodide, vanadium (III) bromide, niobium (V) bromide, molybdenum (V) chloride, and tungsten (VI) chloride, which are rapidly converted to insoluble oxides and hydroxides in the presence of moist air.

Much could be done with coordination compounds having nitrogen or cyanide ligands by way of determining stability constants, coordination numbers, and cis-trans isomerism.

A fairly obvious generalization from the foregoing work is that the relationship between aqueous and ammonia half-wave potentials is largely dependent on solvation energies. Thus, alkali metal compounds are more easily reduced in ammonia, while the converse is true of ammine-coordinating transition metals. In conclusion, the status of liquid ammonia polarography makes it moderately interesting from an analytical viewpoint; and quite promising for future research. To return to the electrical storm analogy of the Preface, it now appears that lightning has struck at several points, and even though droplets continue to fall, damage assessment should begin.

APPENDIX

FIGURE A - I



60
50
40
30
20
10
μa
-1.9
-2.0
-2.1
-2.2
-2.3
VOLTS
LiNO3 10-3 M
IN NH3 , TEAB
Pb:Pb++ REFERENCE

FIGURE A - 2

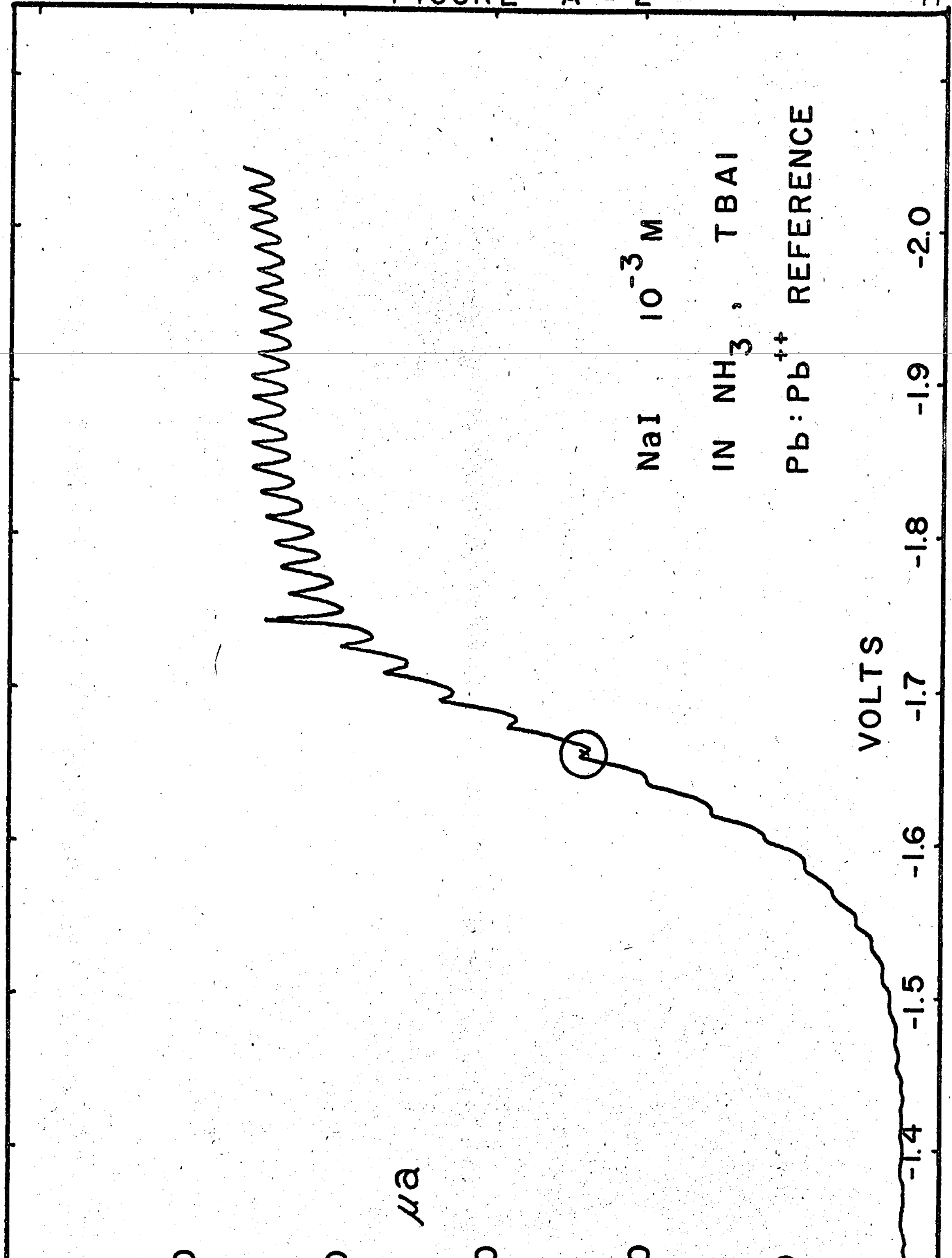

μa
50
40
30
20
10
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
VOLTS
NaI 10^{-3} M
IN NH_3 , TBAI
Pb : Pb^{++} REFERENCE

FIGURE A - 3

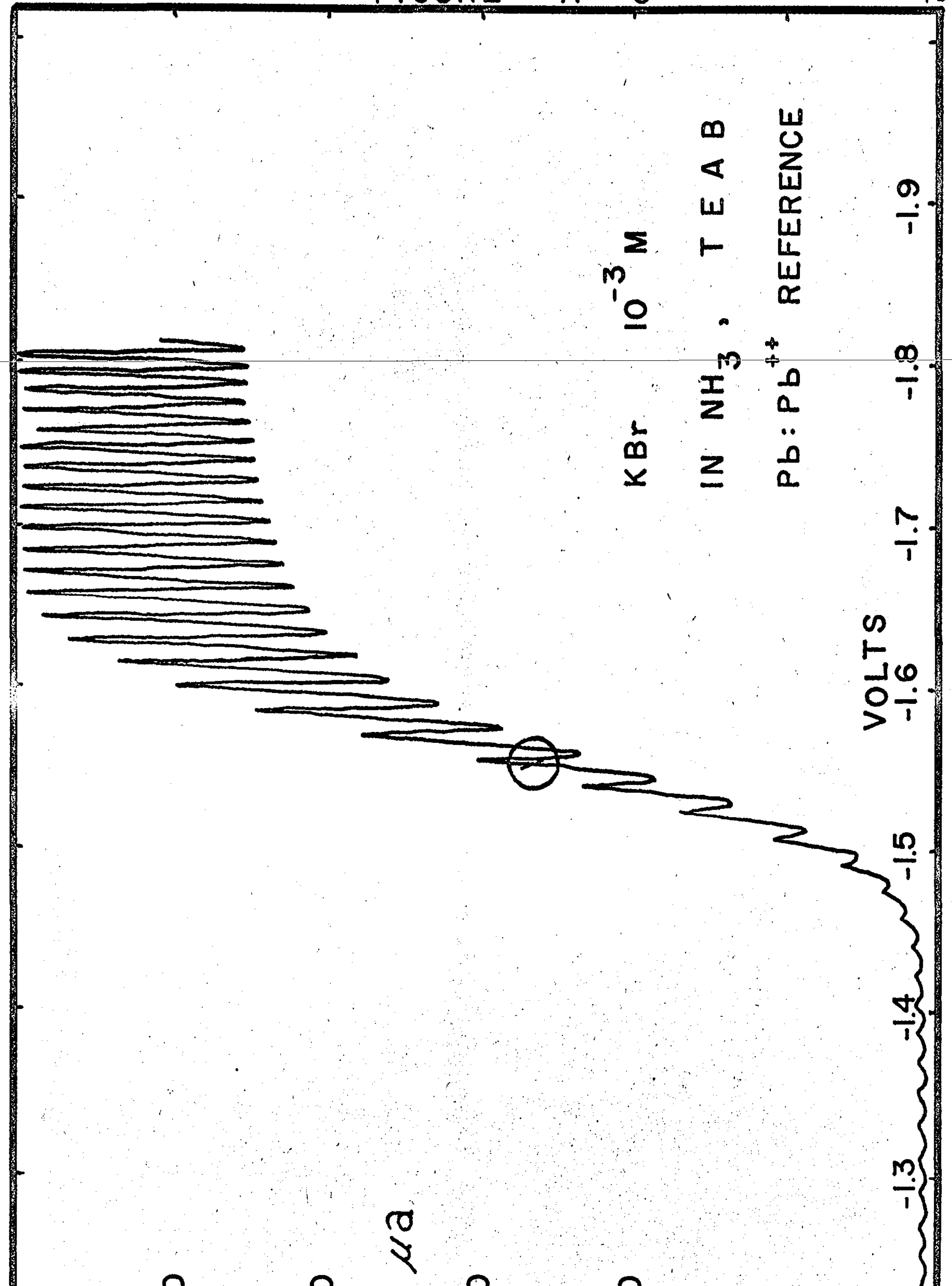

KBr 10^{-3} M
IN NH_3 , T E A B
Pb : Pb^{++} REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
μa
10
20
30
40
50

FIGURE A - 4

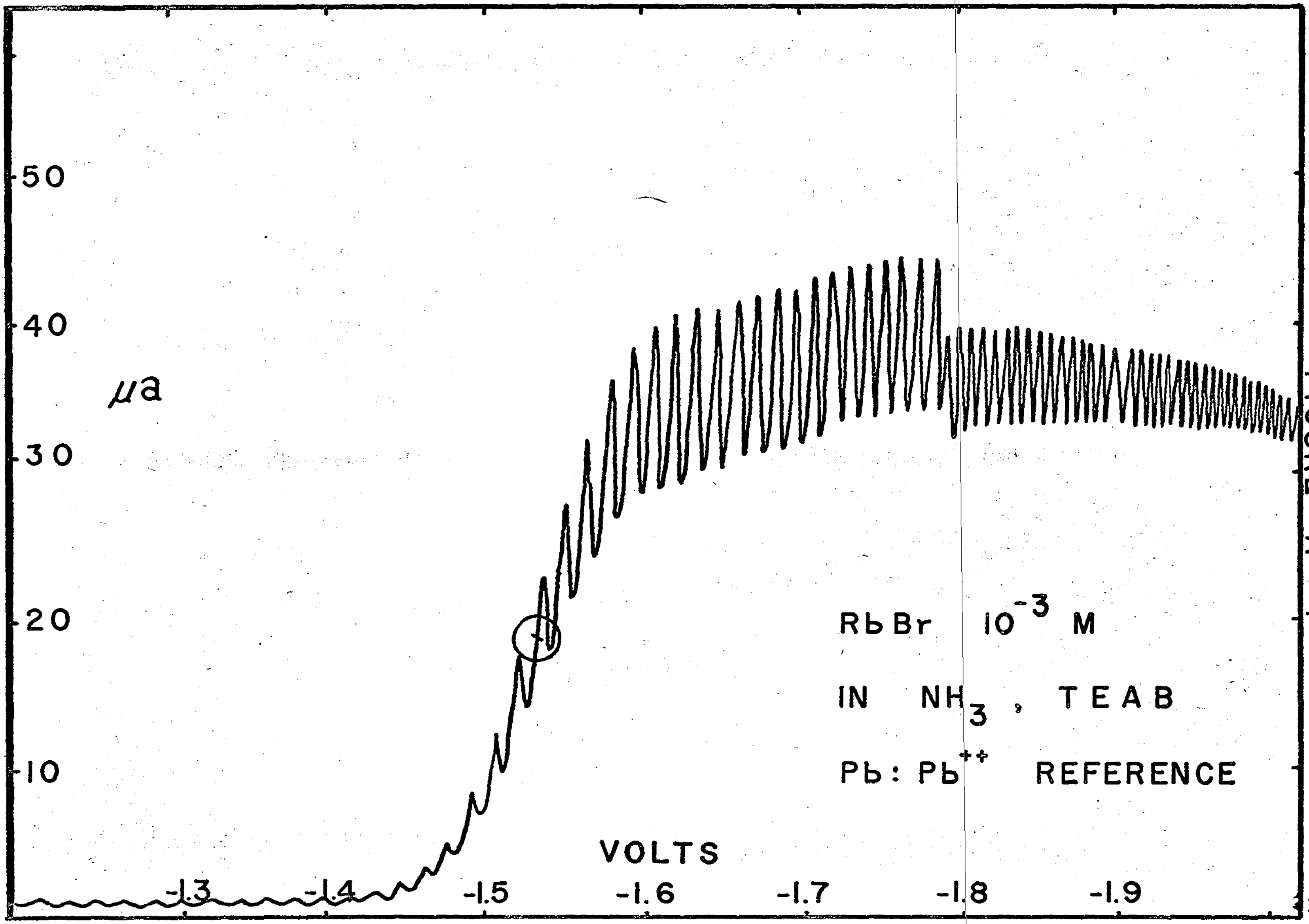

50
40
30
20
10
μa
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
VOLTS
RbBr 10^{-3} M
IN NH_3 , TEAB
Pb : Pb^{++} REFERENCE

FIGURE A - 5

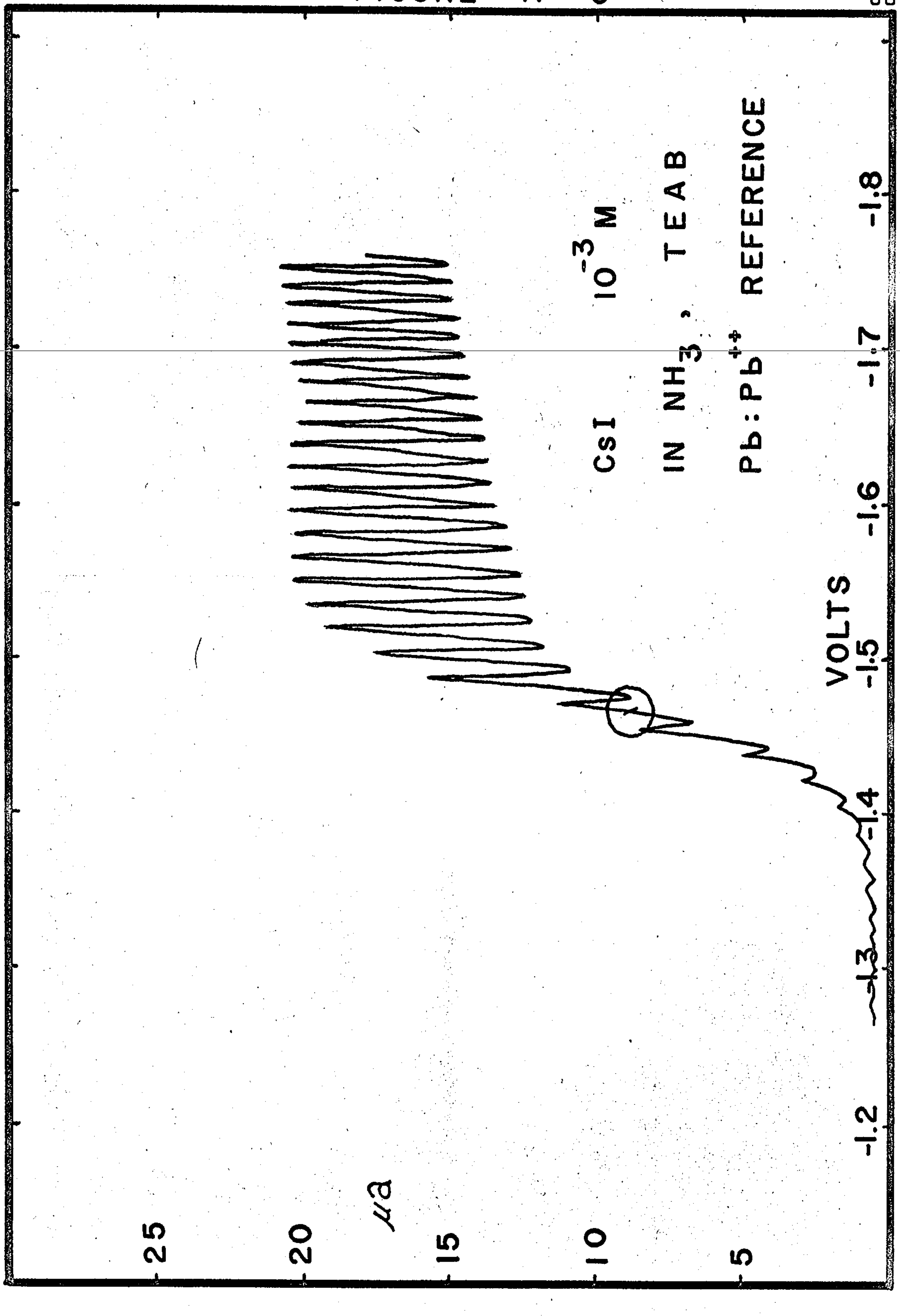

CsI 10^{-3} M
IN NH_3, TEAB
Pb : Pb^{++} REFERENCE
μa
25
20
15
10
5
VOLTS
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8

FIGURE A - 6

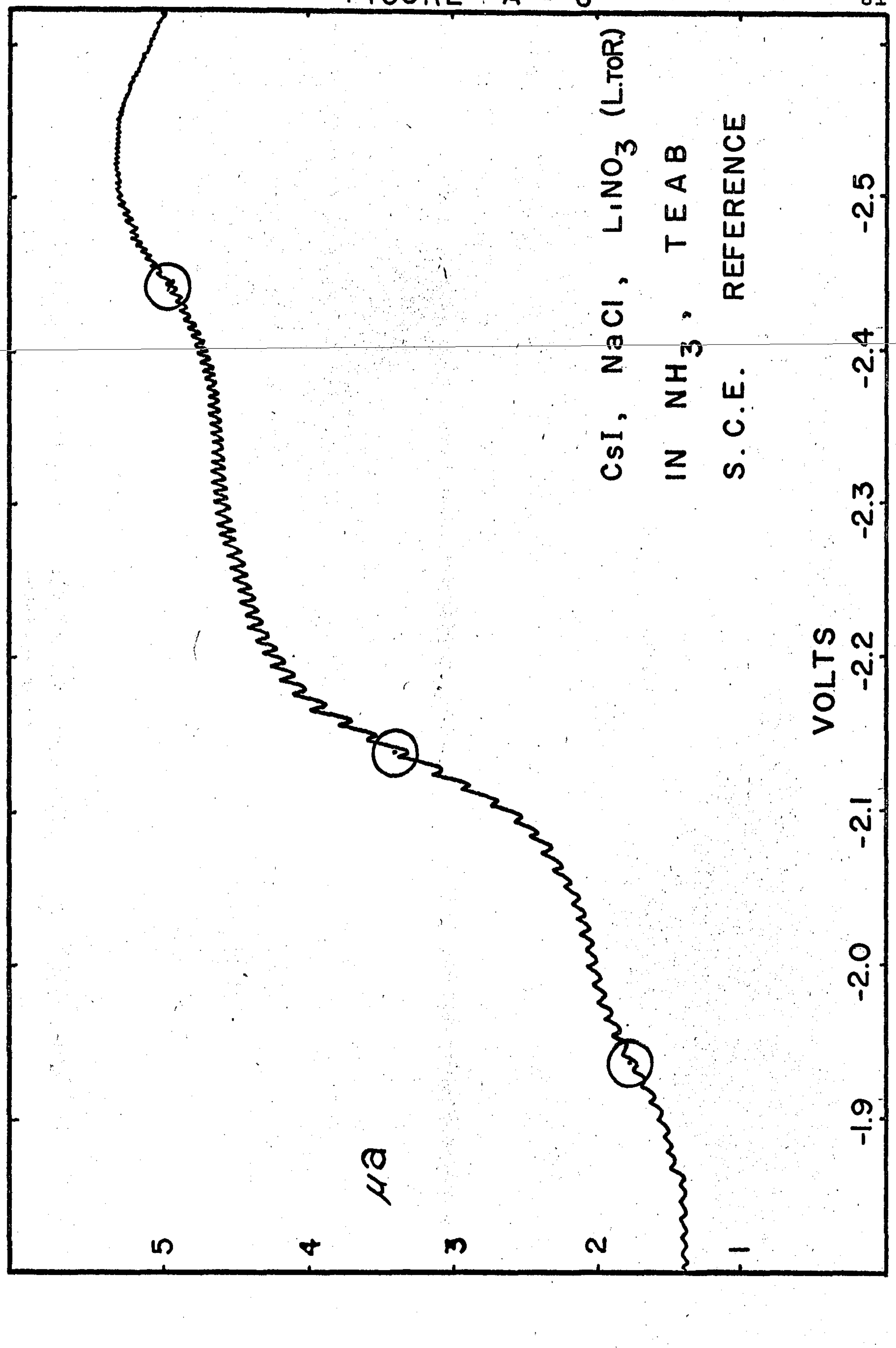
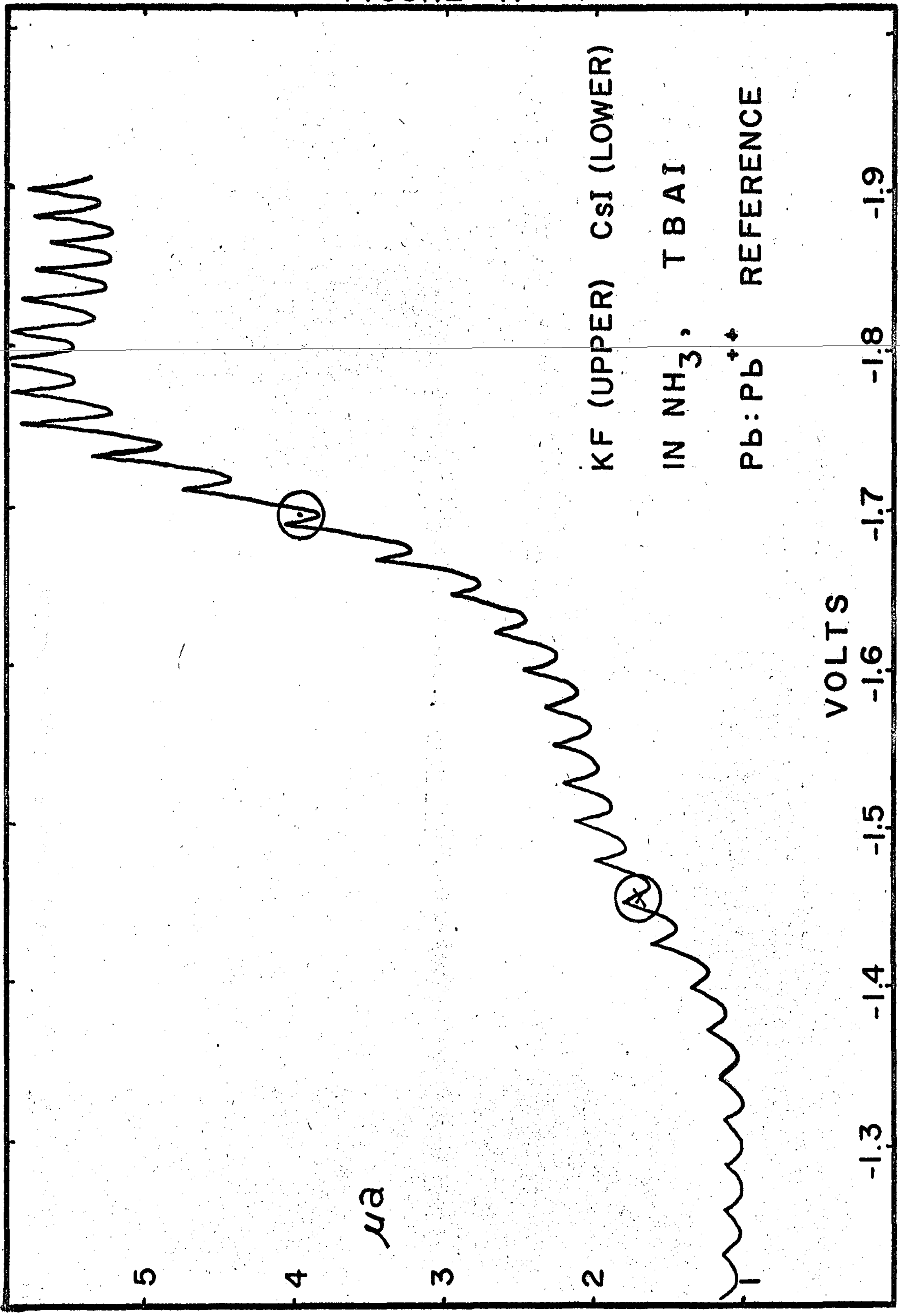

CsI, NaCl, LiNO$_3$ (L. TO R.)
IN NH$_3$, TEAB
S.C.E. REFERENCE
VOLTS
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4
-2.5
μa
1
2
3
4
5

FIGURE A - 7


KF (UPPER) CsI (LOWER)
IN NH_3, TBAI
$Pb:Pb^{++}$ REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
μa
5
4
3
2
1

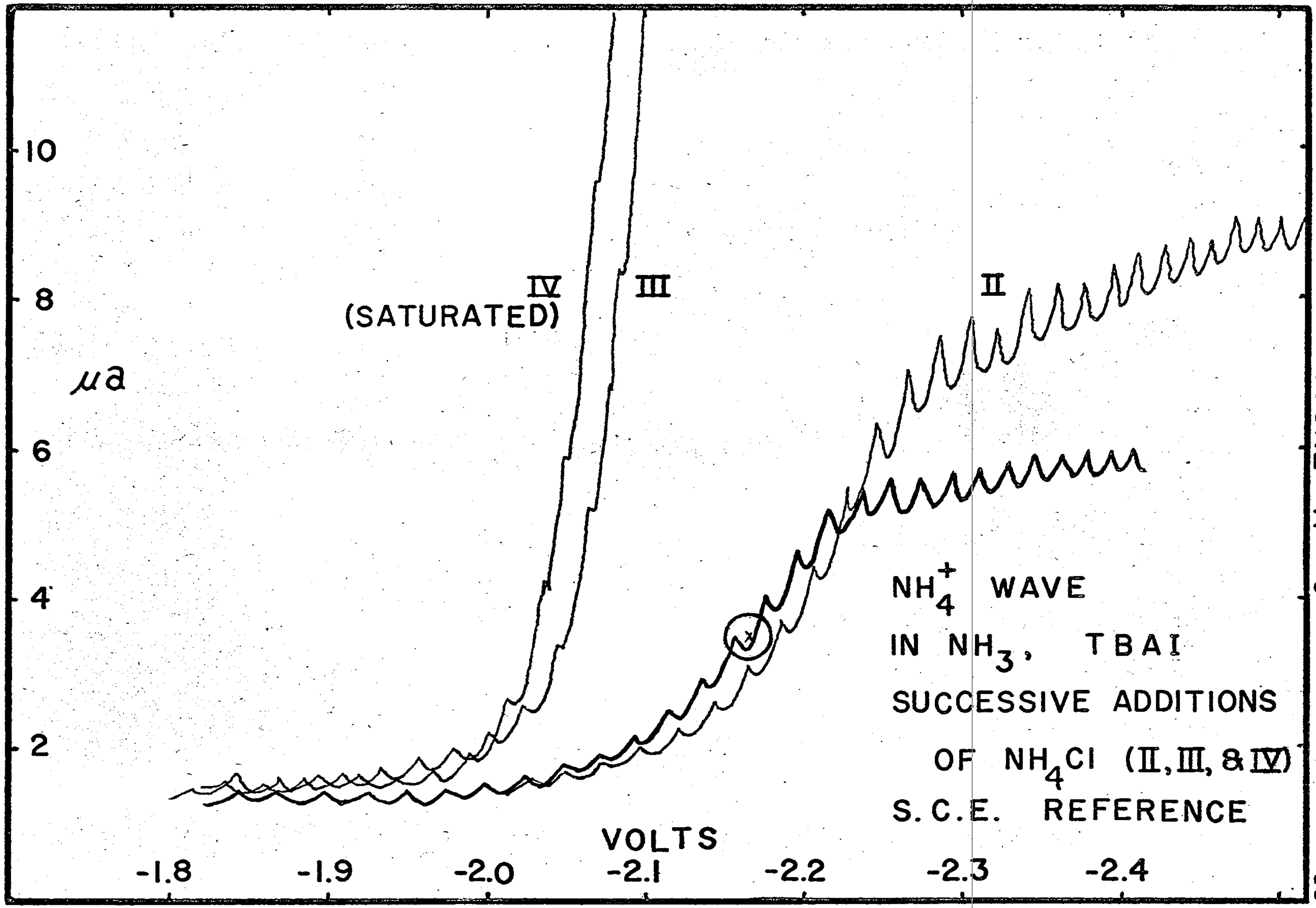

IV
(SATURATED)
III
II
μa
10
8
6
4
2
VOLTS
-1.8
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4
NH_4^+ WAVE
IN NH_3, TBAI
SUCCESSIVE ADDITIONS
OF NH_4Cl (II, III, & IV)
S.C.E. REFERENCE

FIGURE A-8

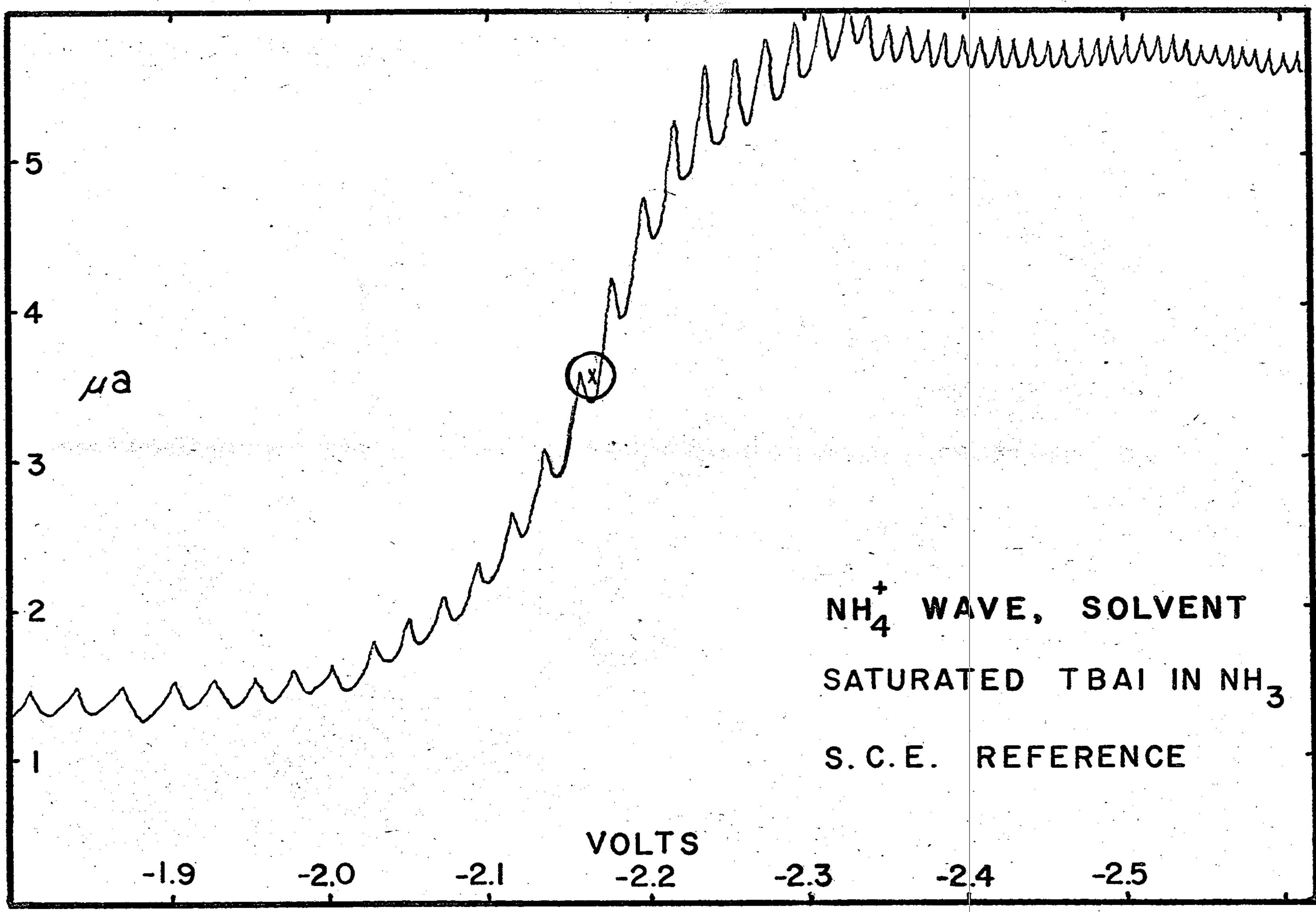
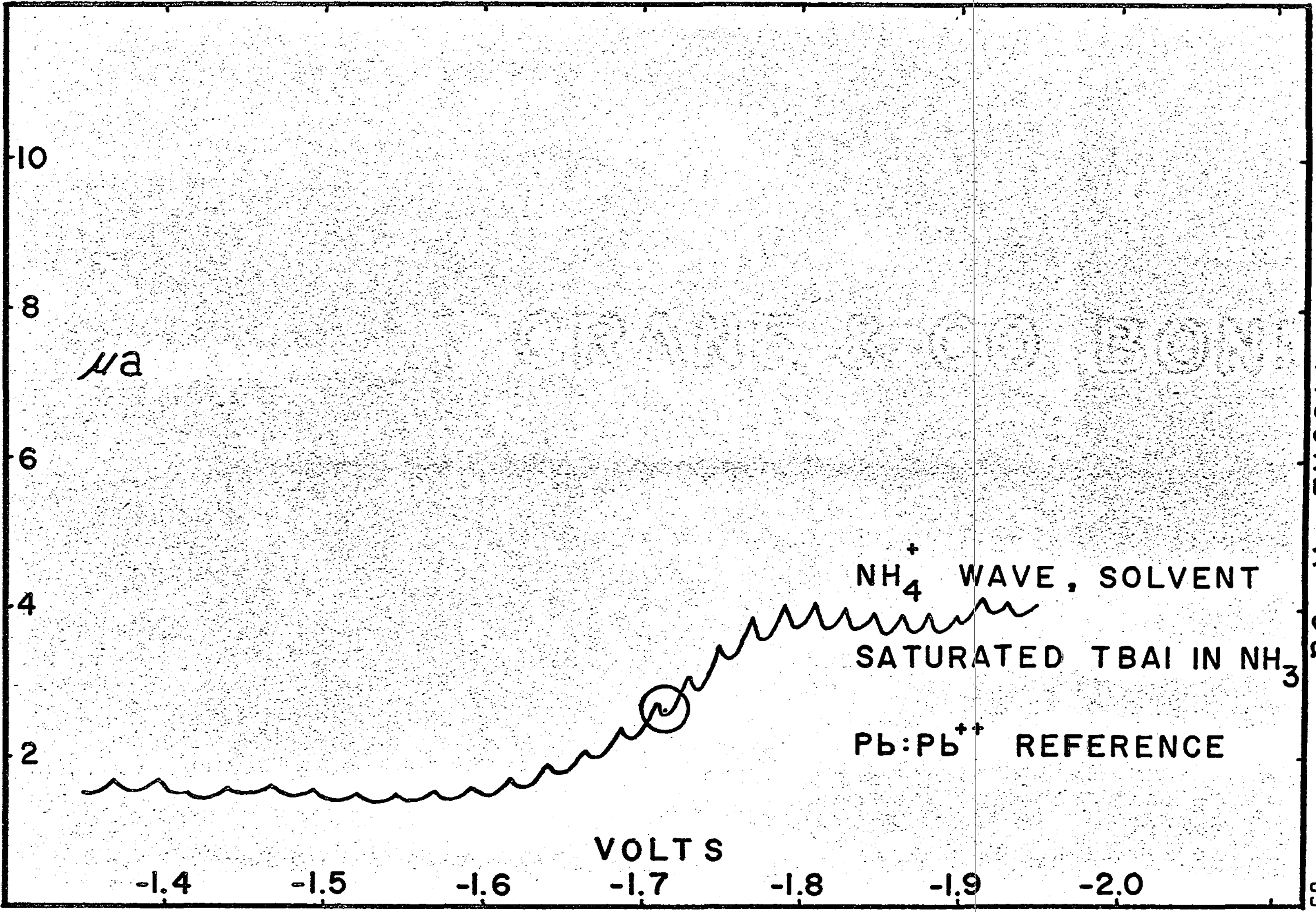

μa
5
4
3
2
1
VOLTS
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4
-2.5
x
NH_4^+ WAVE, SOLVENT
SATURATED TBAI IN NH_3
S.C.E. REFERENCE

FIGURE A-9

FIGURE A - 9a



μa
10
8
6
4
2
NH_4^+ WAVE, SOLVENT
SATURATED TBAI IN NH_3
$Pb:Pb^{++}$ REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0

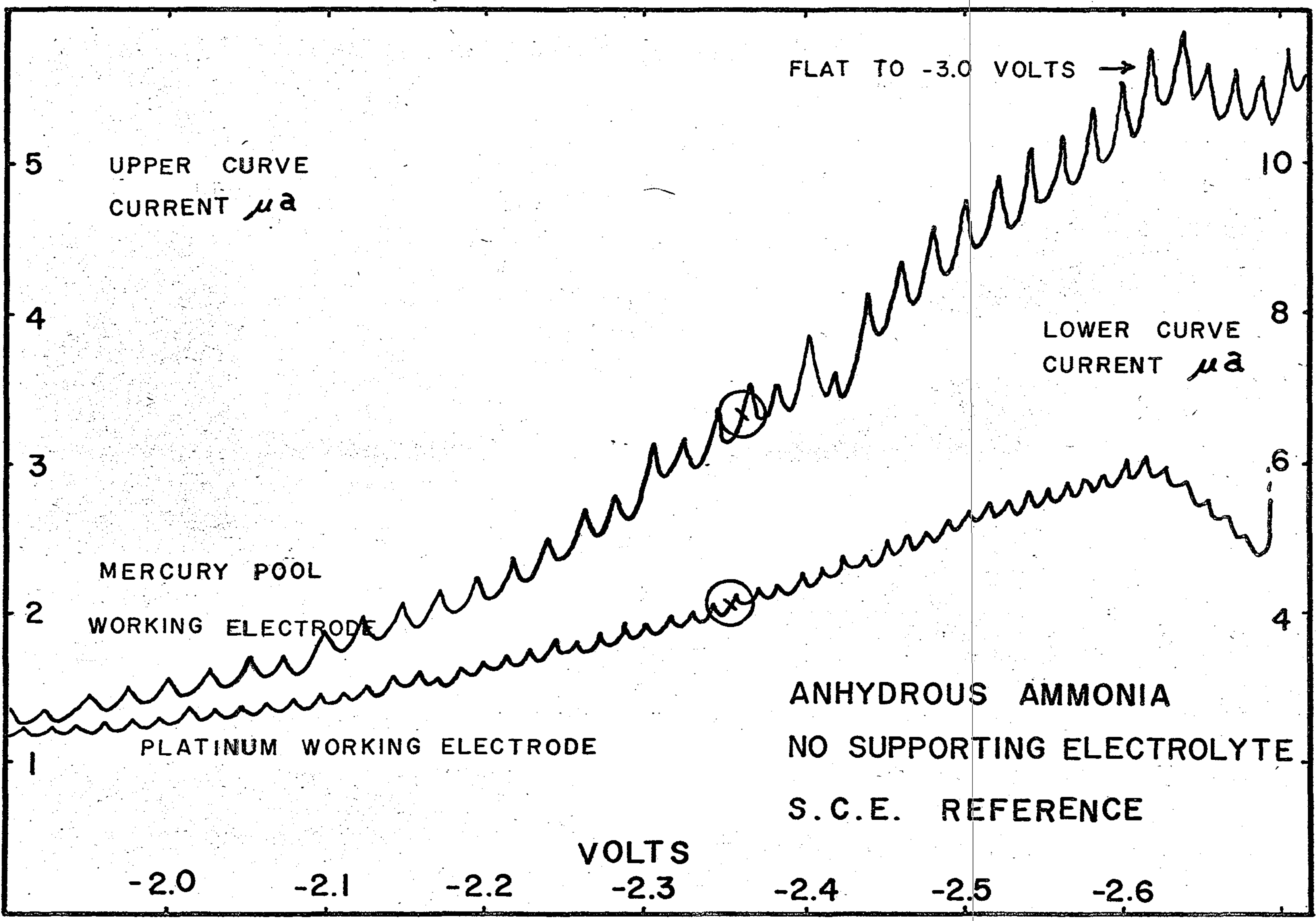

FLAT TO -3.0 VOLTS →
UPPER CURVE
CURRENT μa
5
4
3
2
1
10
8
6
4
LOWER CURVE
CURRENT μa
MERCURY POOL
WORKING ELECTRODE
PLATINUM WORKING ELECTRODE
ANHYDROUS AMMONIA
NO SUPPORTING ELECTROLYTE
S.C.E. REFERENCE
VOLTS
-2.0
-2.1
-2.2
-2.3
-2.4
-2.5
-2.6

FIGURE A-10

FIGURE A - 11

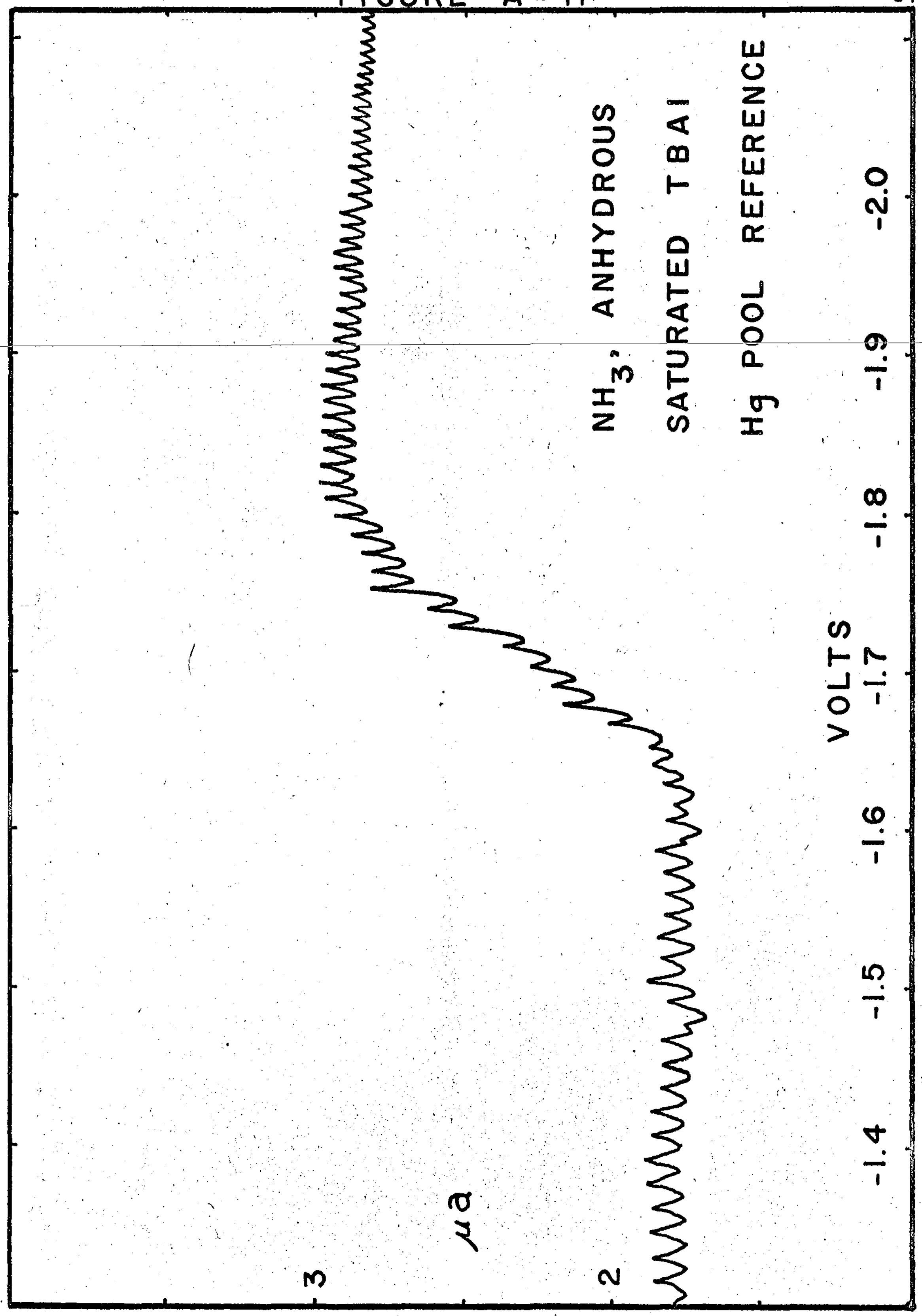

NH$_3$, ANHYDROUS
SATURATED TBAI
Hg POOL REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
3
2

FIGURE A - 12

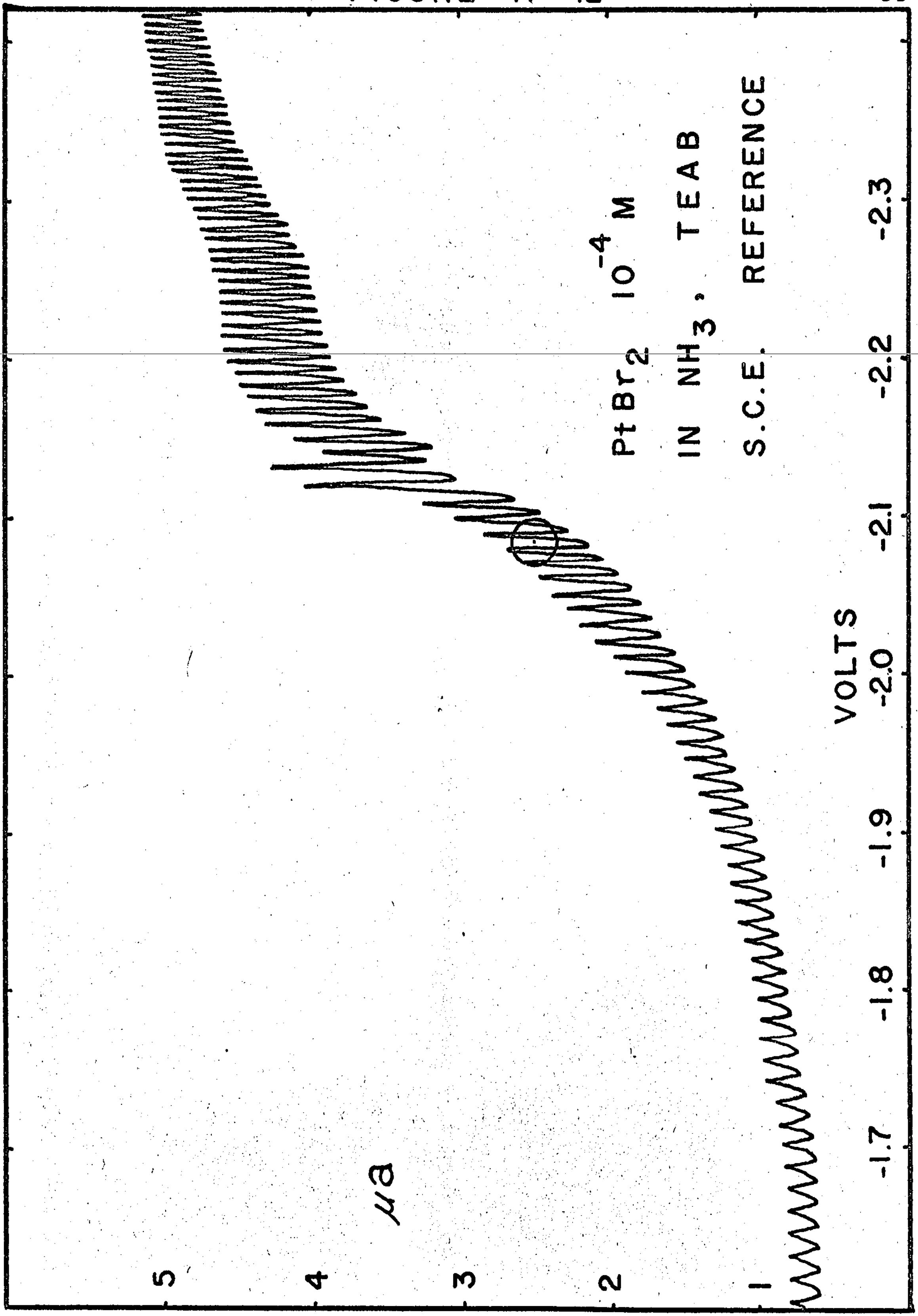
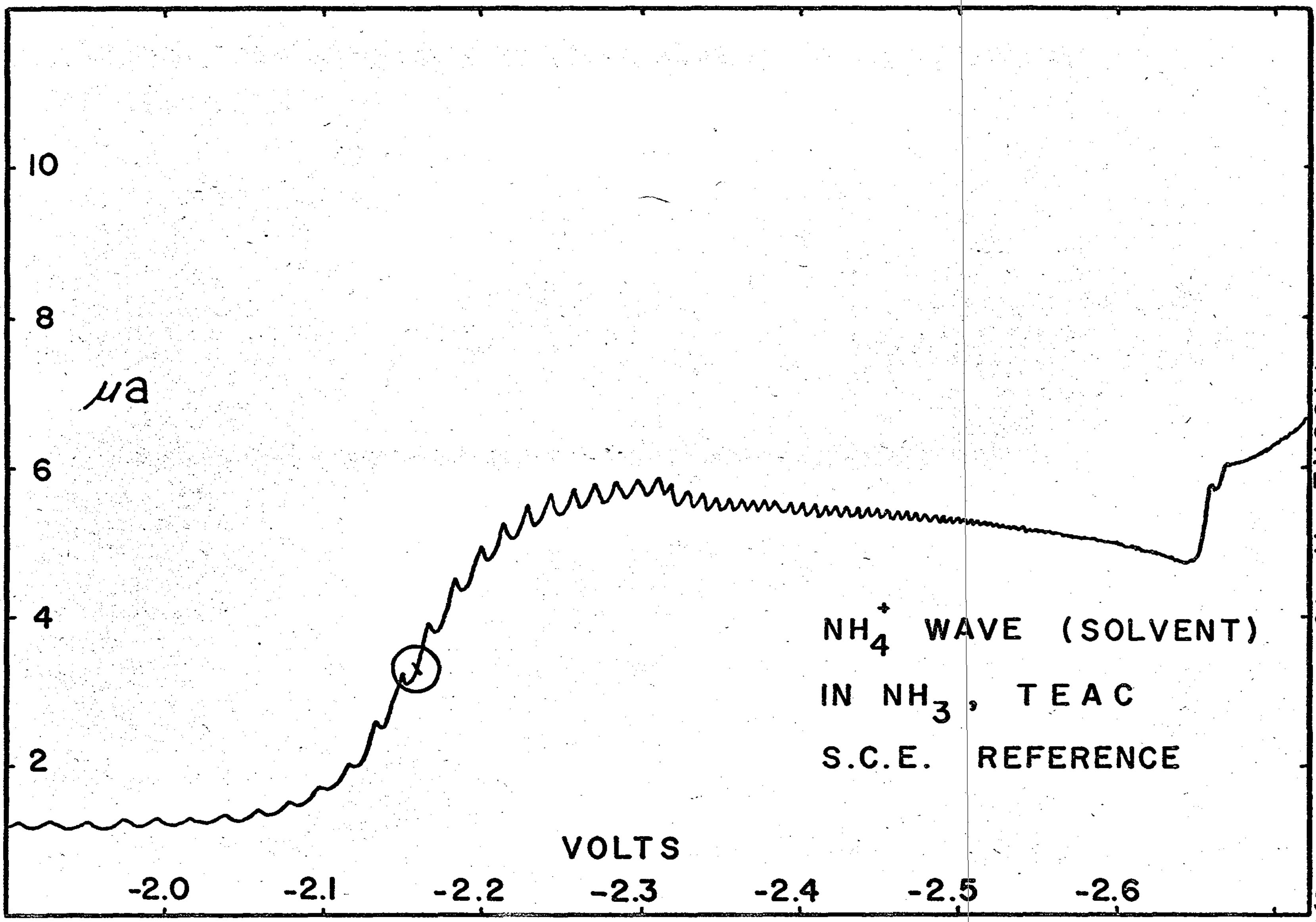

PtBr$_2$ 10^{-4} M
IN NH$_3$, TEAB
S.C.E. REFERENCE
VOLTS
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
-2.3
μa
1
2
3
4
5

FIGURE A-13


NH$_4^+$ WAVE (SOLVENT)
IN NH$_3$, TEAC
S.C.E. REFERENCE
μa
10
8
6
4
2
VOLTS
-2.0
-2.1
-2.2
-2.3
-2.4
-2.5
-2.6

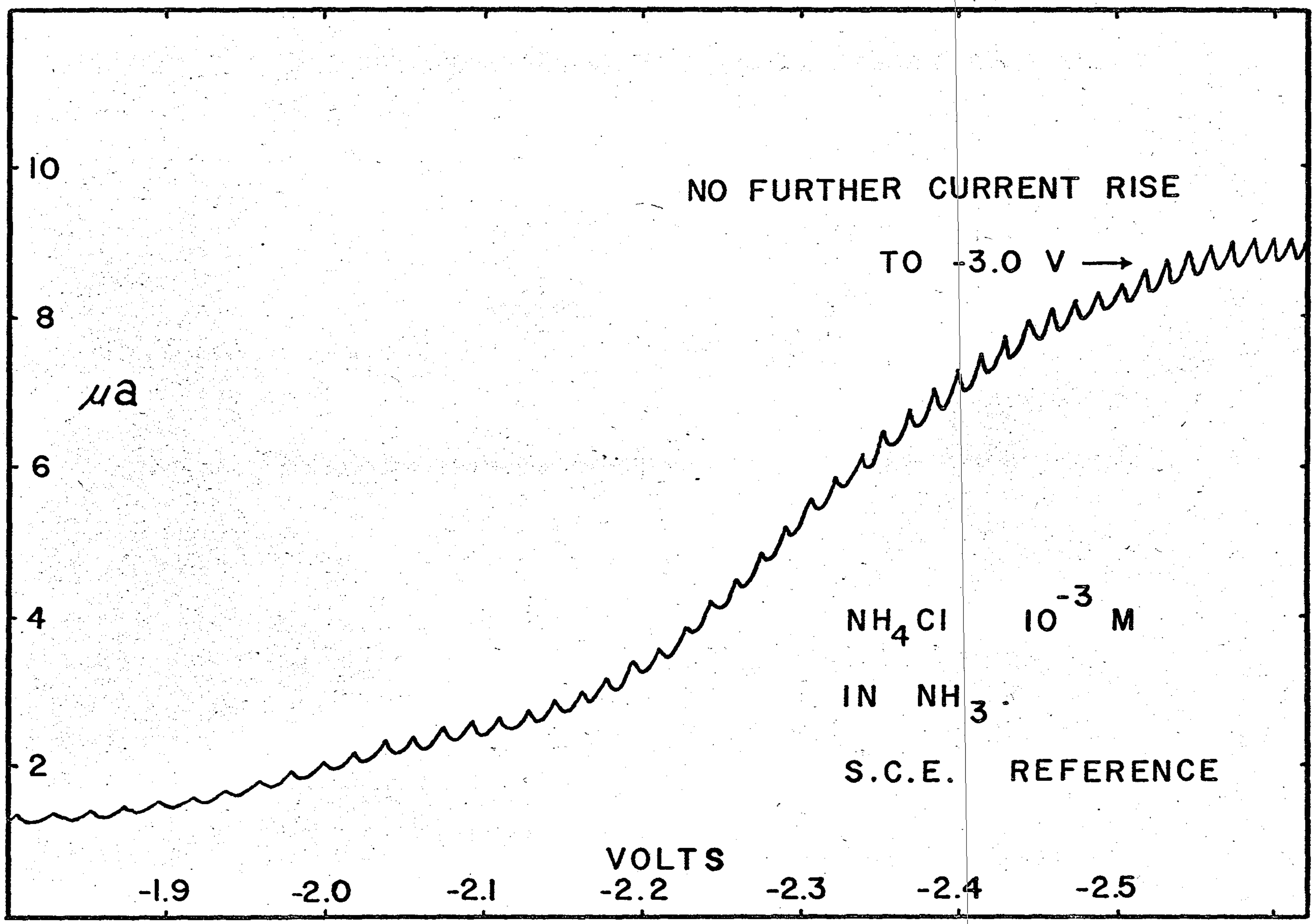

10
8
6
4
2
μa
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4
-2.5
VOLTS
NO FURTHER CURRENT RISE
TO -3.0 V →
NH_4Cl 10^{-3} M
IN NH_3
S.C.E. REFERENCE

FIGURE A-14

FIGURE A - 15

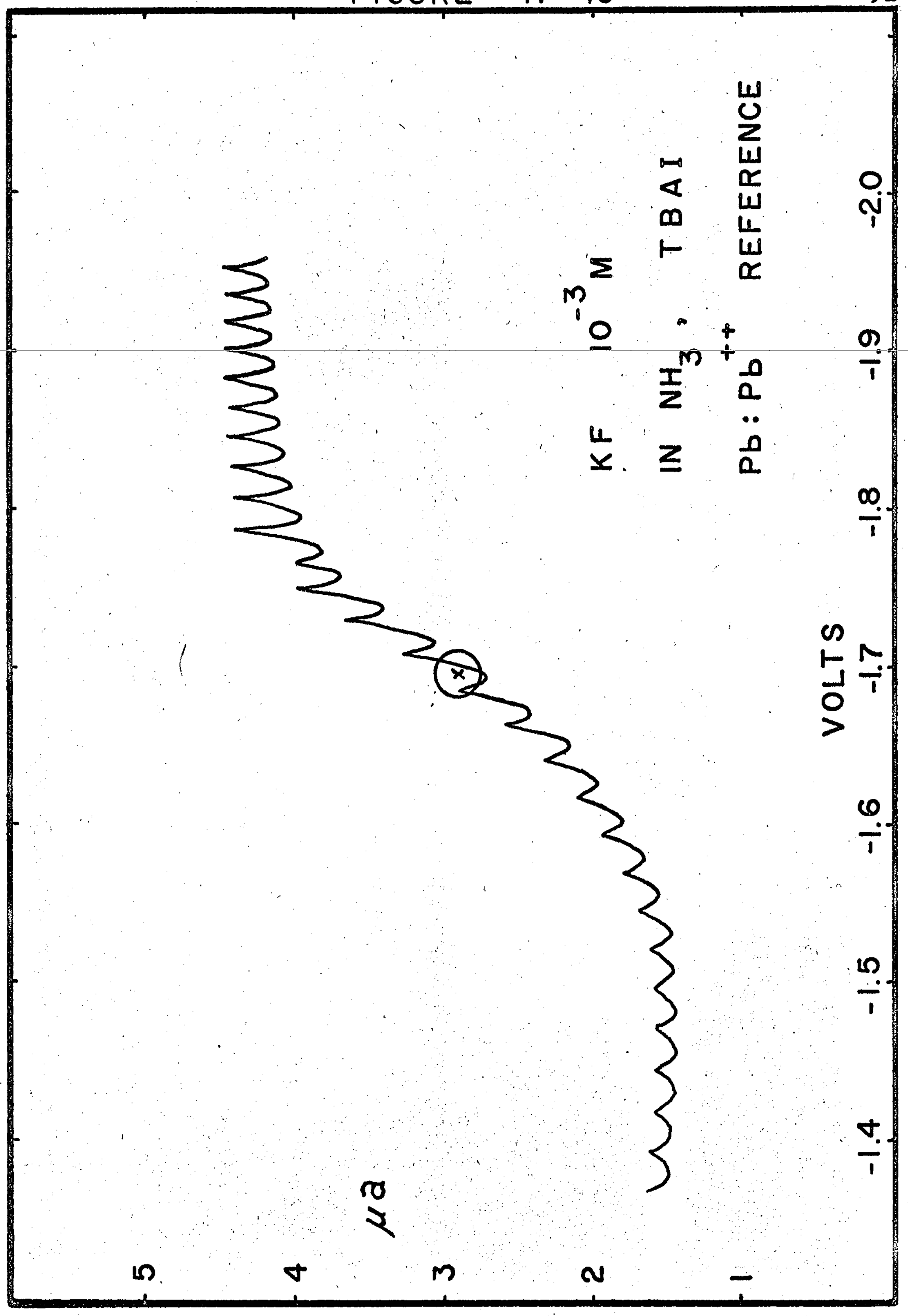
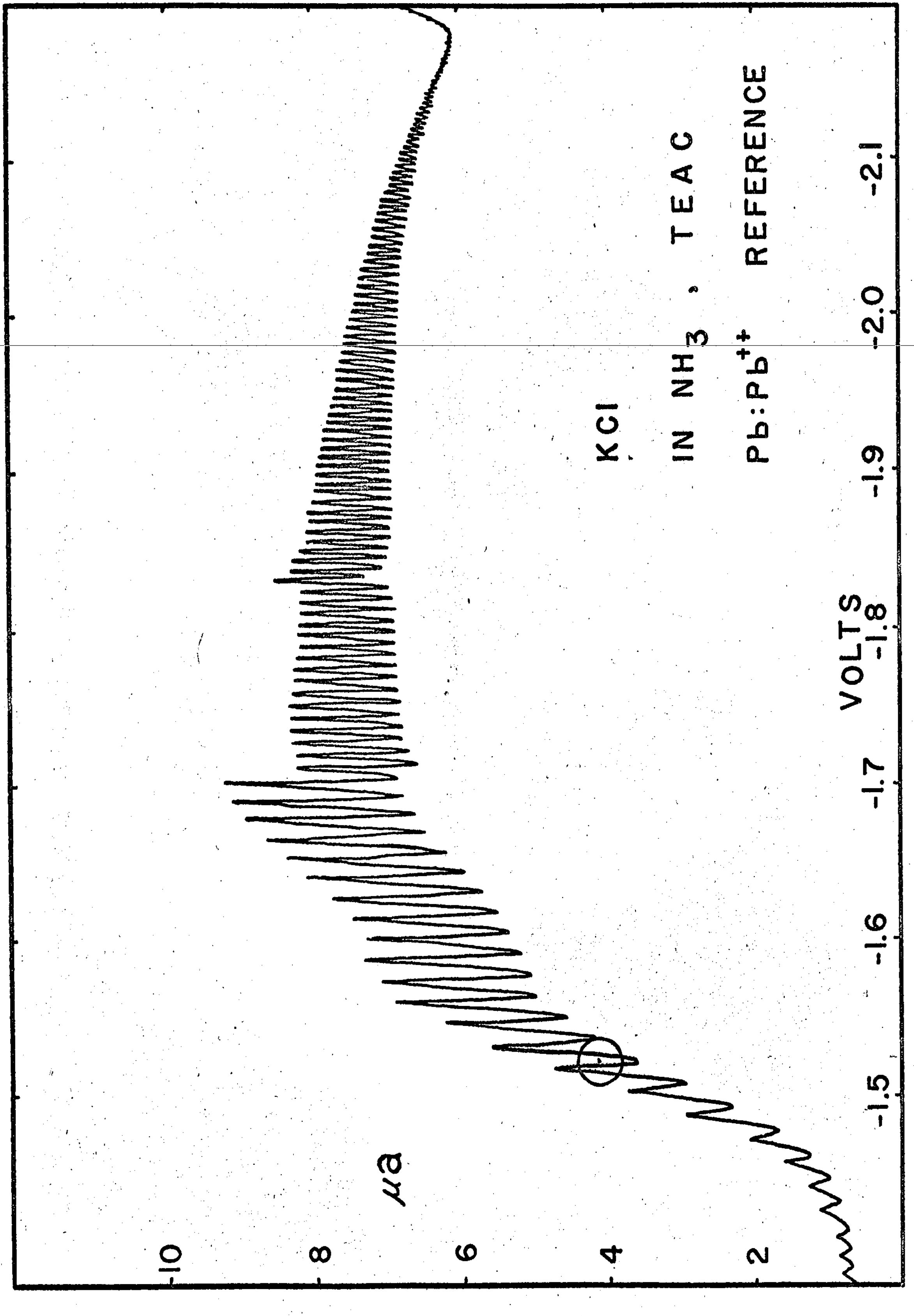

KF 10^{-3} M
IN NH_3 , TBAI
Pb : Pb^{++} REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
1
2
3
4
5

FIGURE A-16


μa
10
8
6
4
2
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
VOLTS
KCl
IN NH$_3$, TEAC
Pb:Pb^{++} REFERENCE

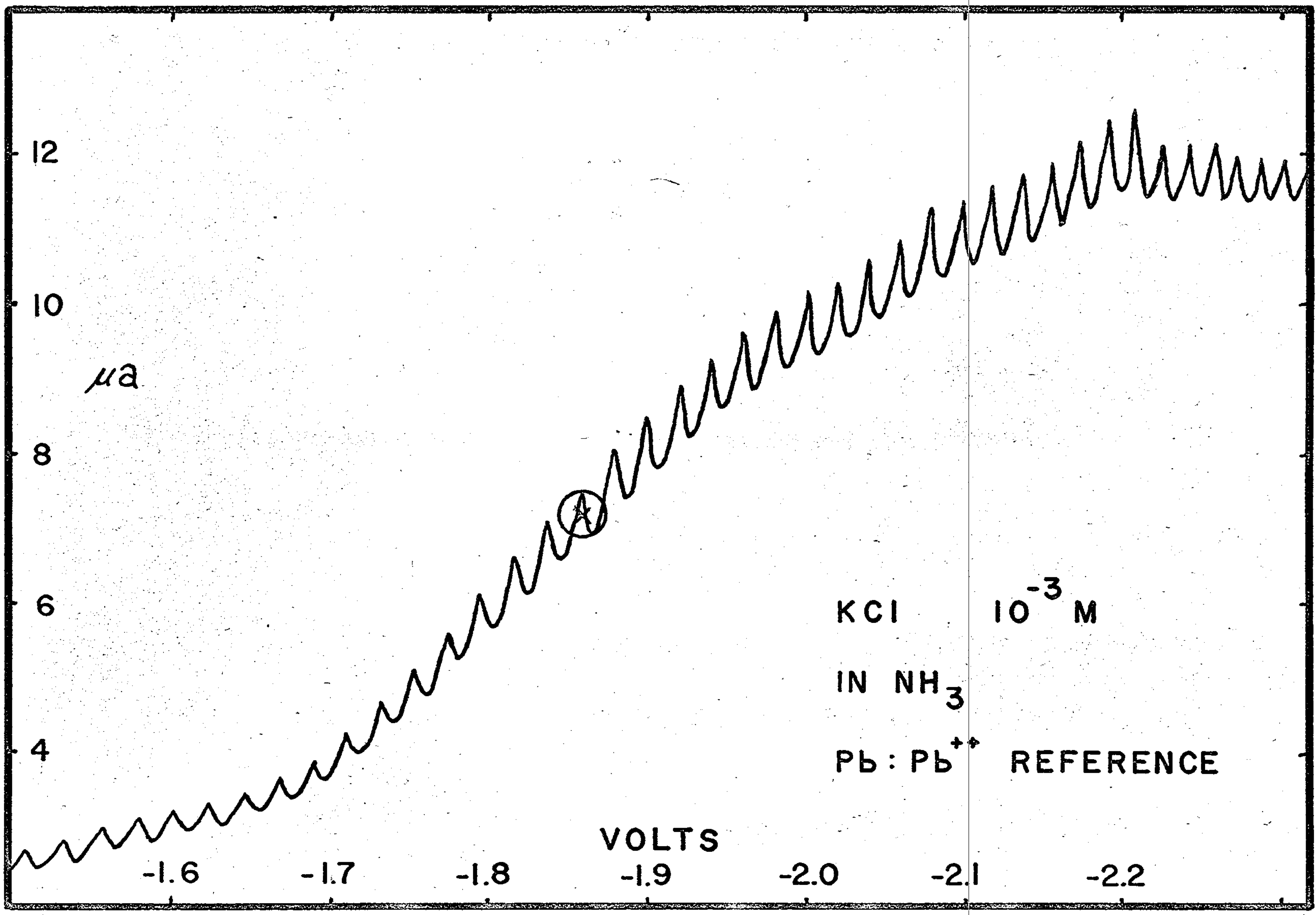

12
10
8
6
4
μa
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
VOLTS
KCl 10^{-3} M
IN NH$_3$
Pb : Pb^{++} REFERENCE

FIGURE A - 16a

FIGURE A - 17

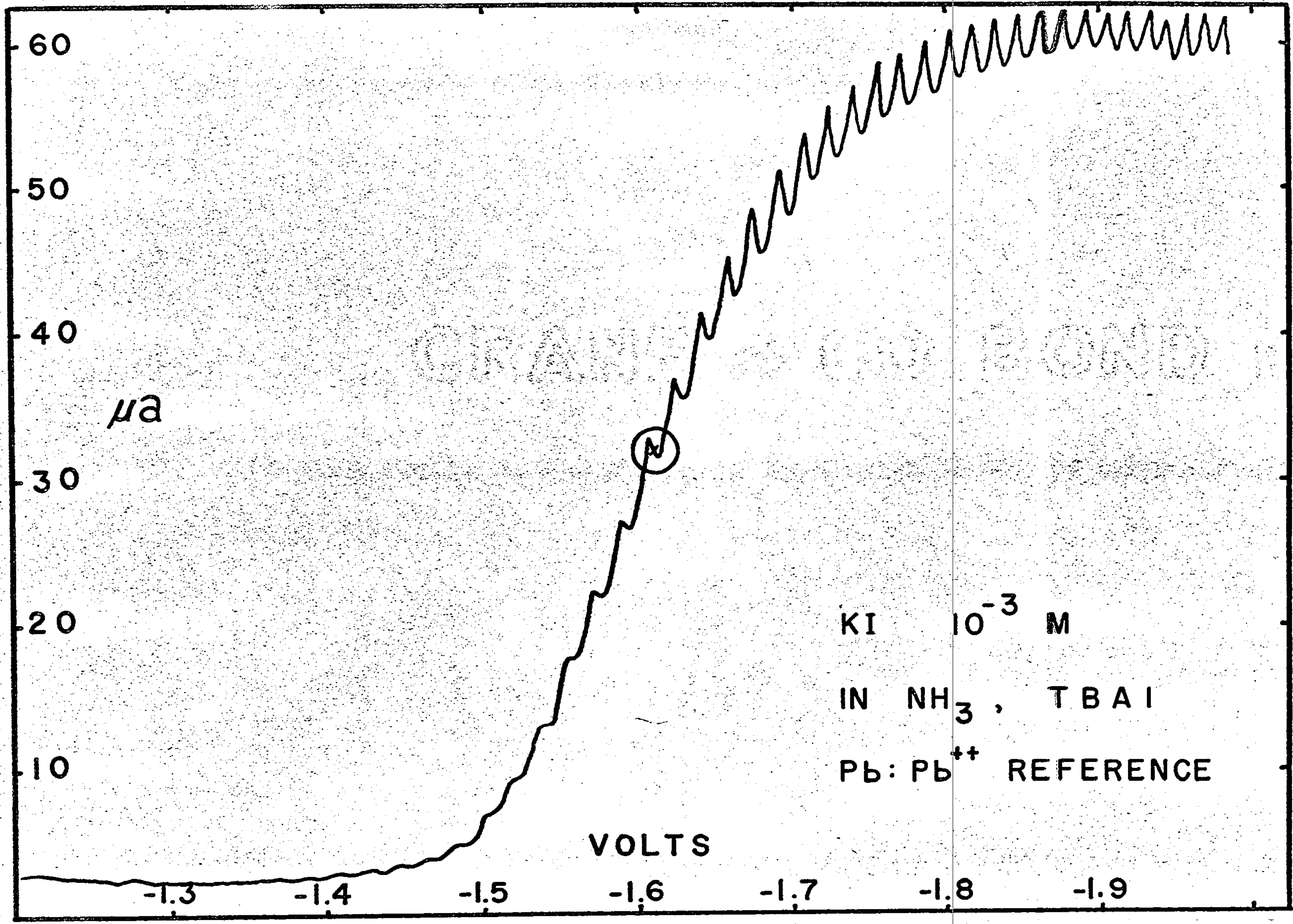
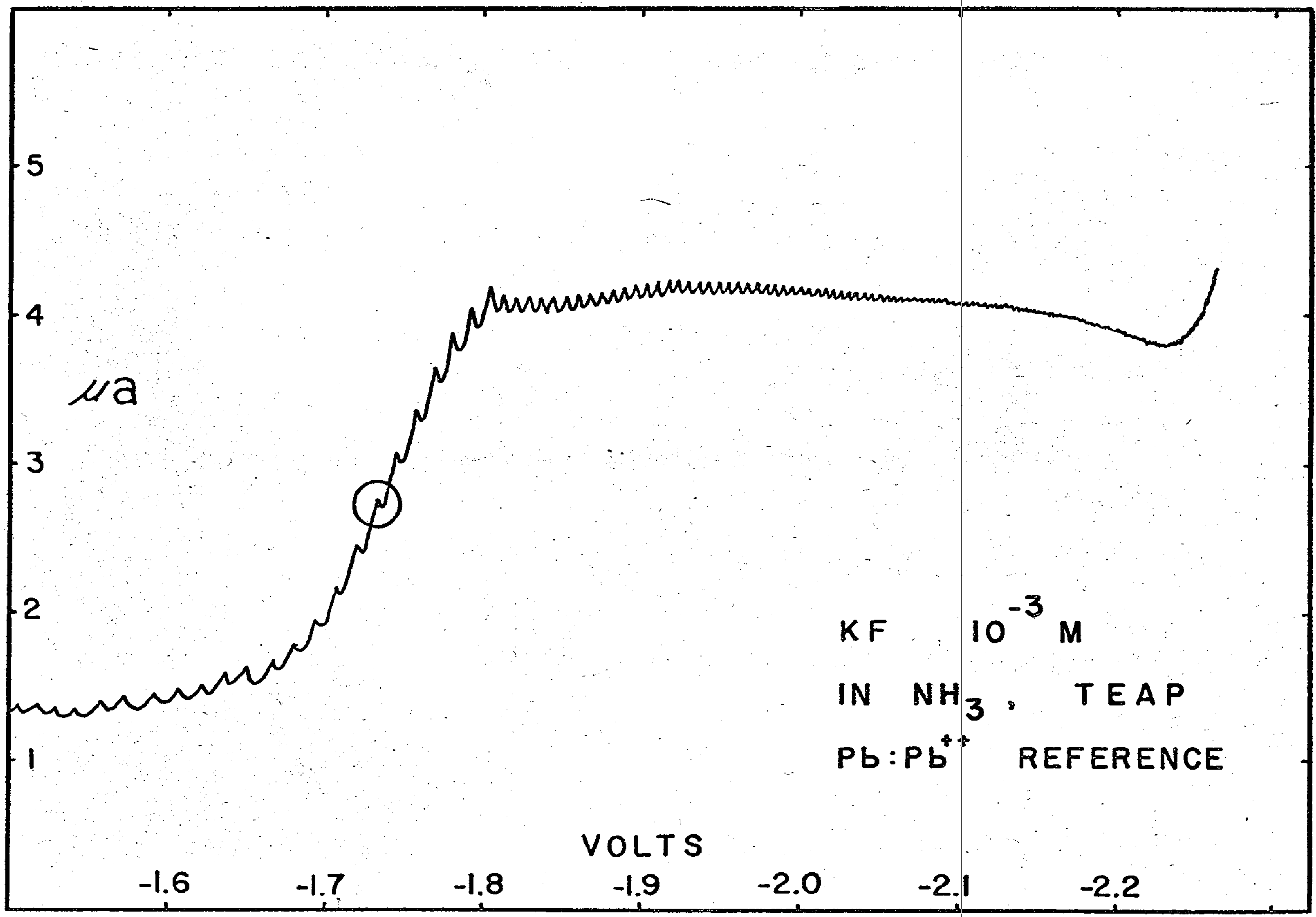

60
50
40
30
20
10
μa
2
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
KI 10^{-3} M
IN NH_3, TBAI
Pb: Pb^{++} REFERENCE

FIGURE A-18


μa
5
4
3
2
1
VOLTS
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
KF 10^{-3} M
IN NH_3, TEAP
$Pb:Pb^{++}$ REFERENCE

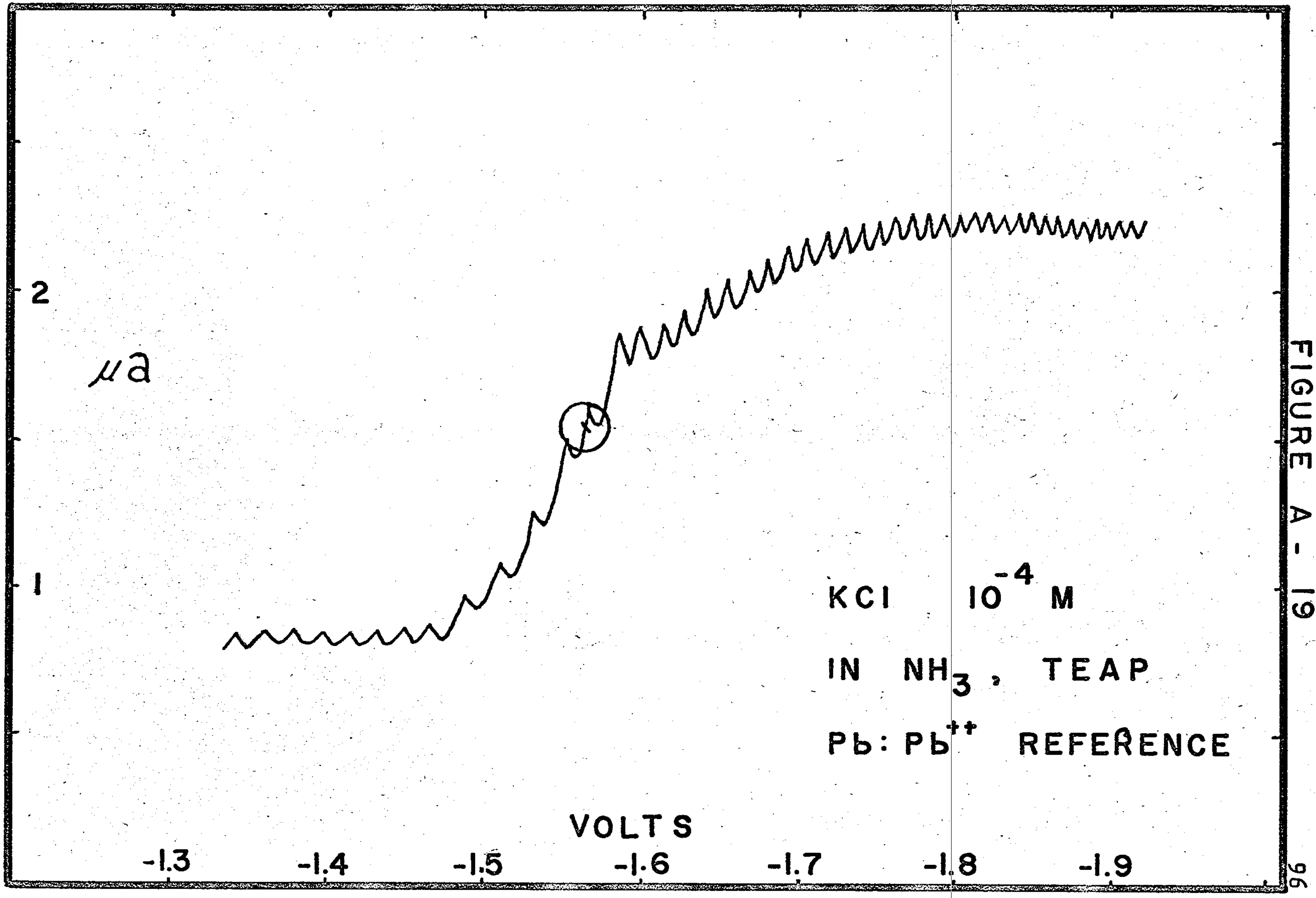

μa
2
1
KCl 10^{-4} M
IN NH_3, TEAP
Pb: Pb^{++} REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9

FIGURE A - 19

FIGURE A-20

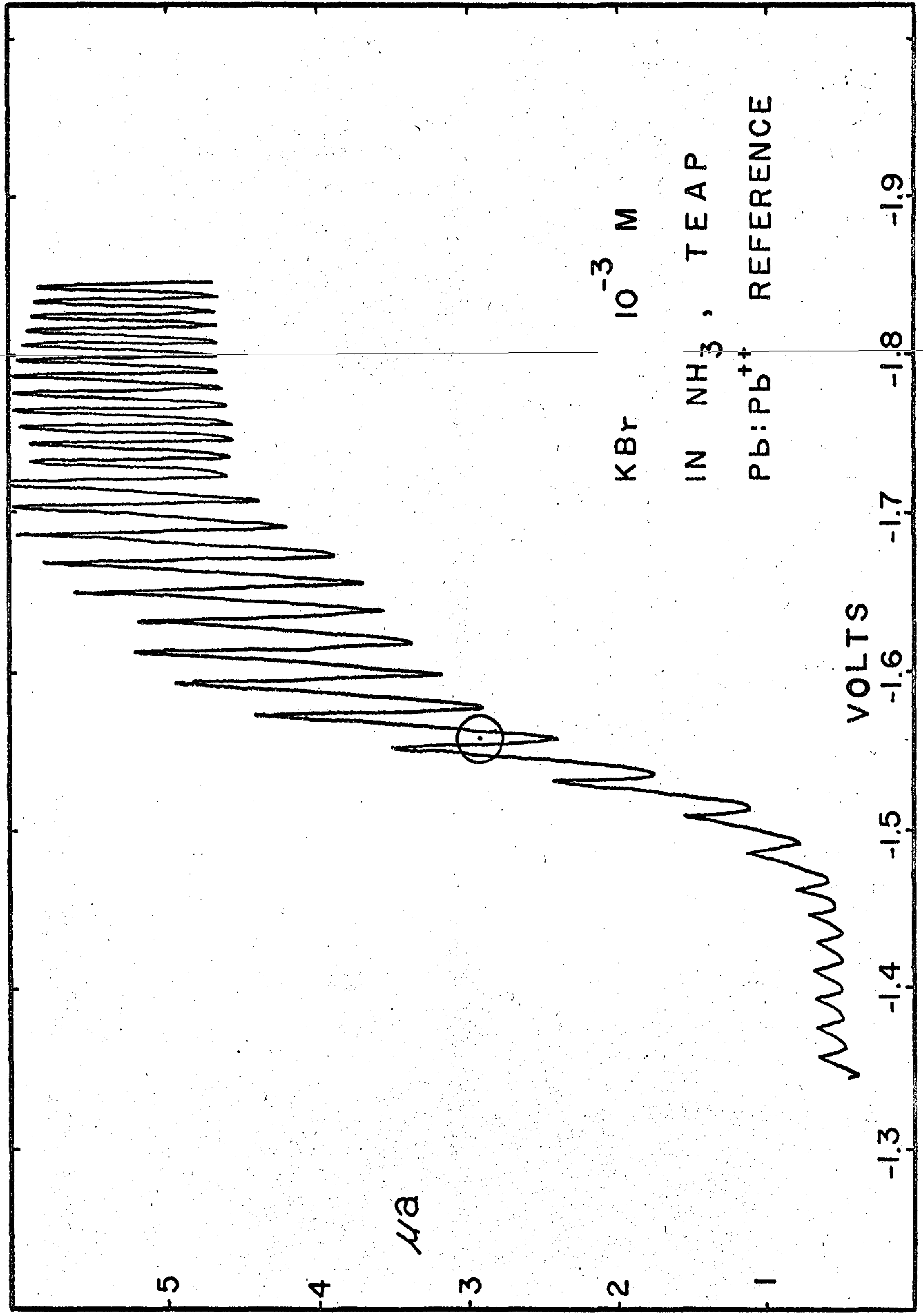

KBr 10^{-3} M
IN NH_3, TEAP
$Pb:Pb^{++}$ REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
μa
1
2
3
4
5

FIGURE A-21

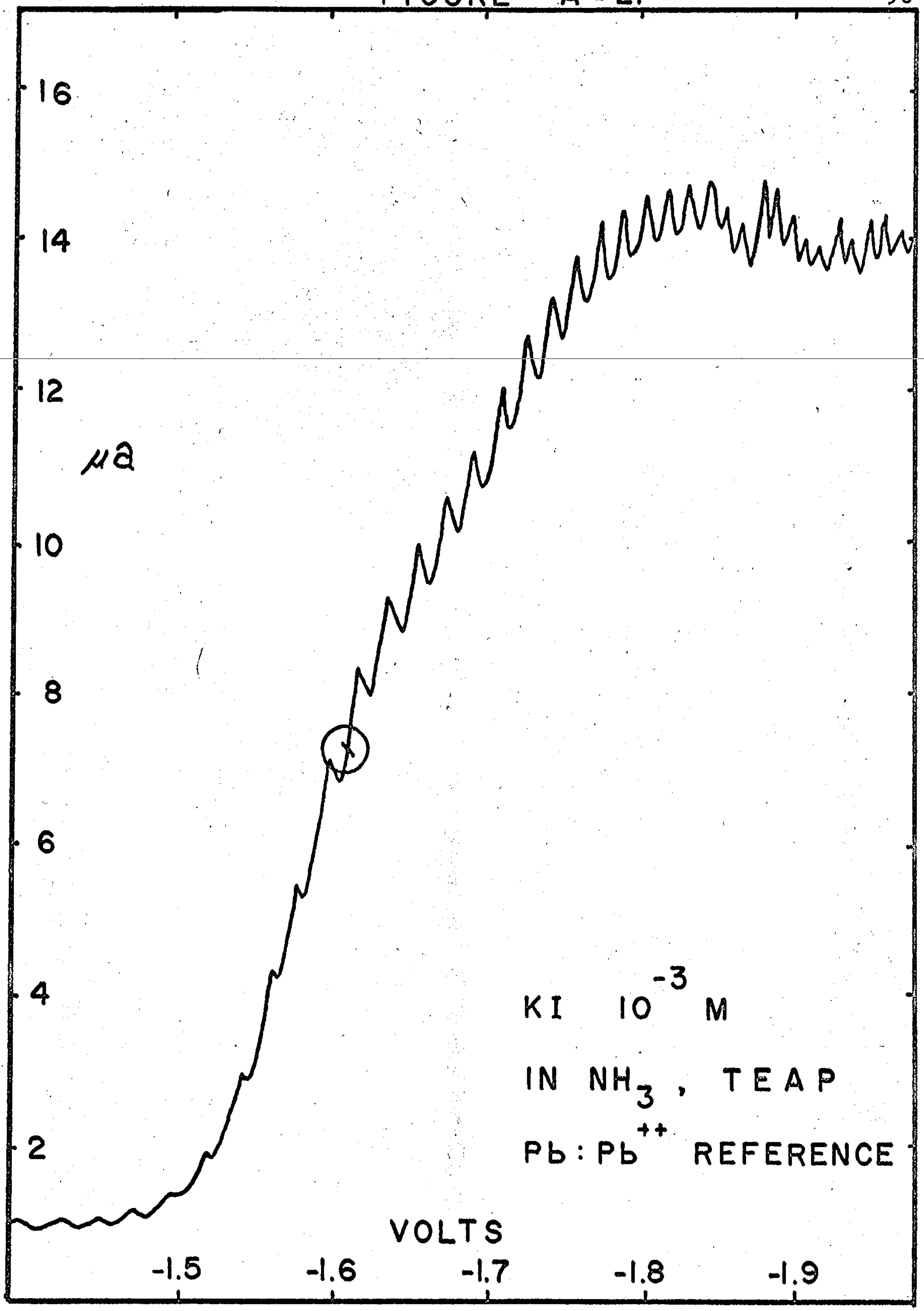

16
14
12
μa
10
8
6
4
2
KI 10^{-3} M
IN NH_3, TEAP
Pb : Pb^{++} REFERENCE
VOLTS
-1.5
-1.6
-1.7
-1.8
-1.9

FIGURE A - 22

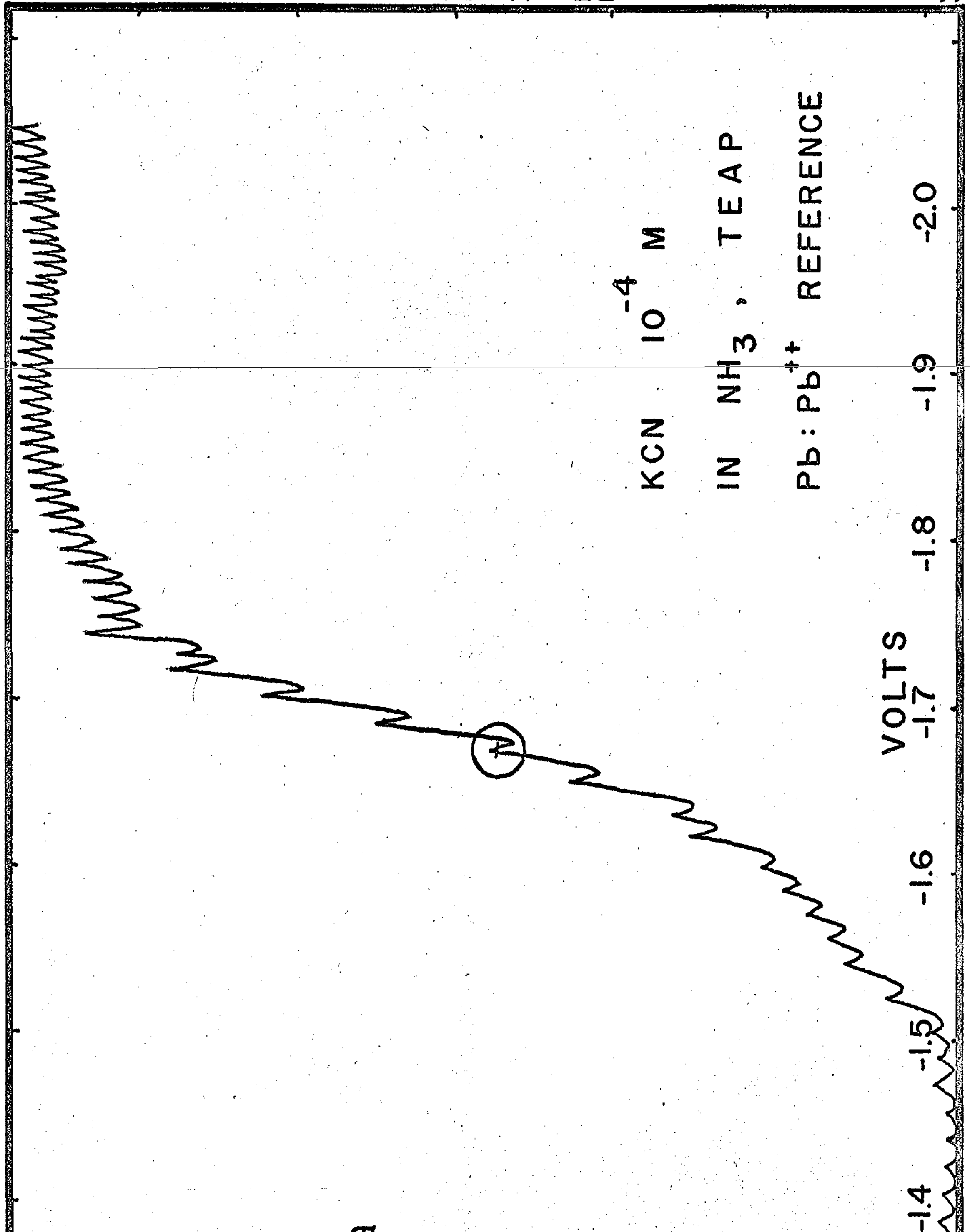

KCN 10^{-4} M
IN NH_3, TEAP
Pb : Pb^{++} REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
1
2
3

FIGURE A - 23

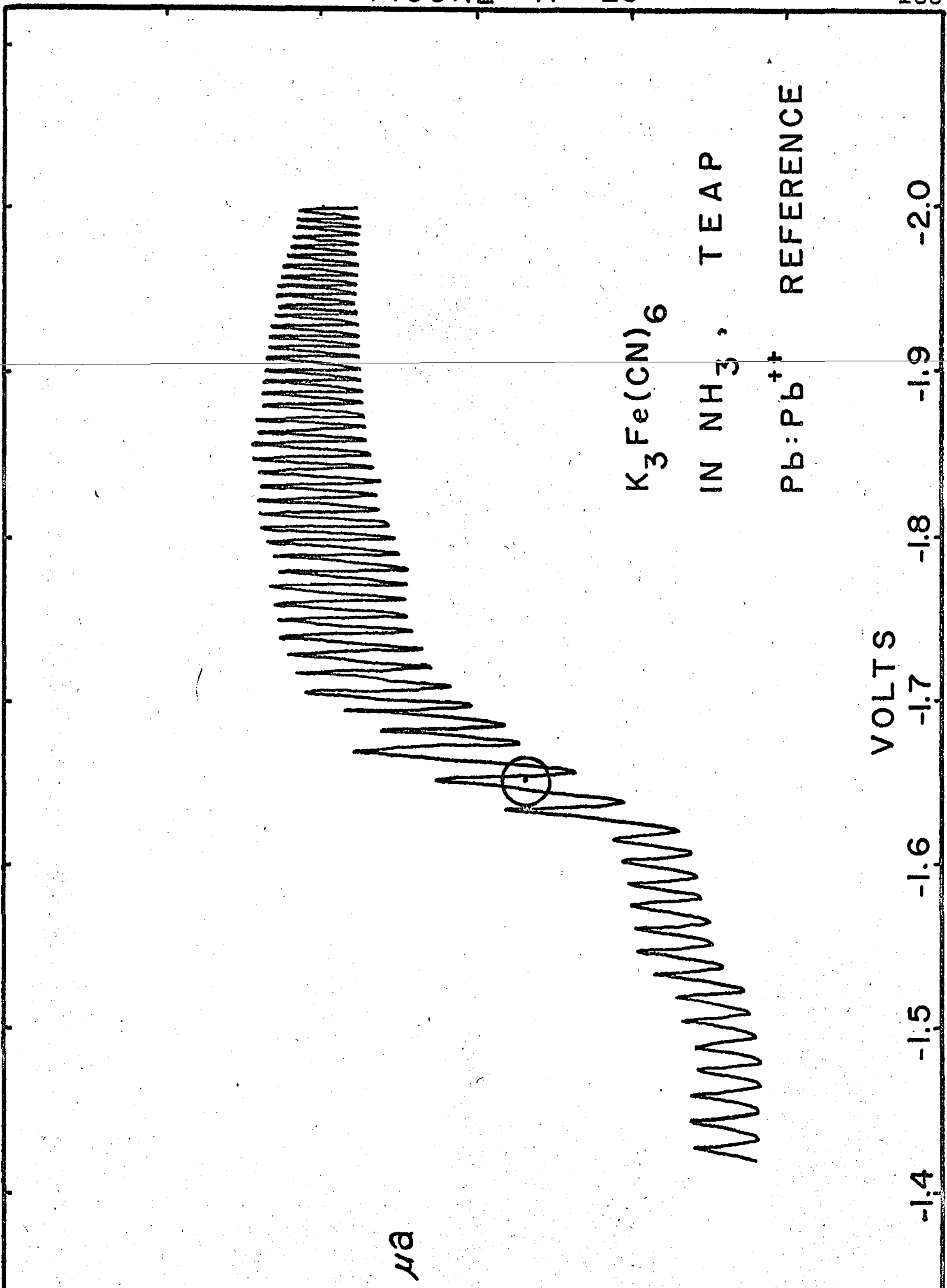

$K_3Fe(CN)_6$
IN NH_3, TEAP
$Pb:Pb^{++}$ REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
2
1

FIGURE A - 24

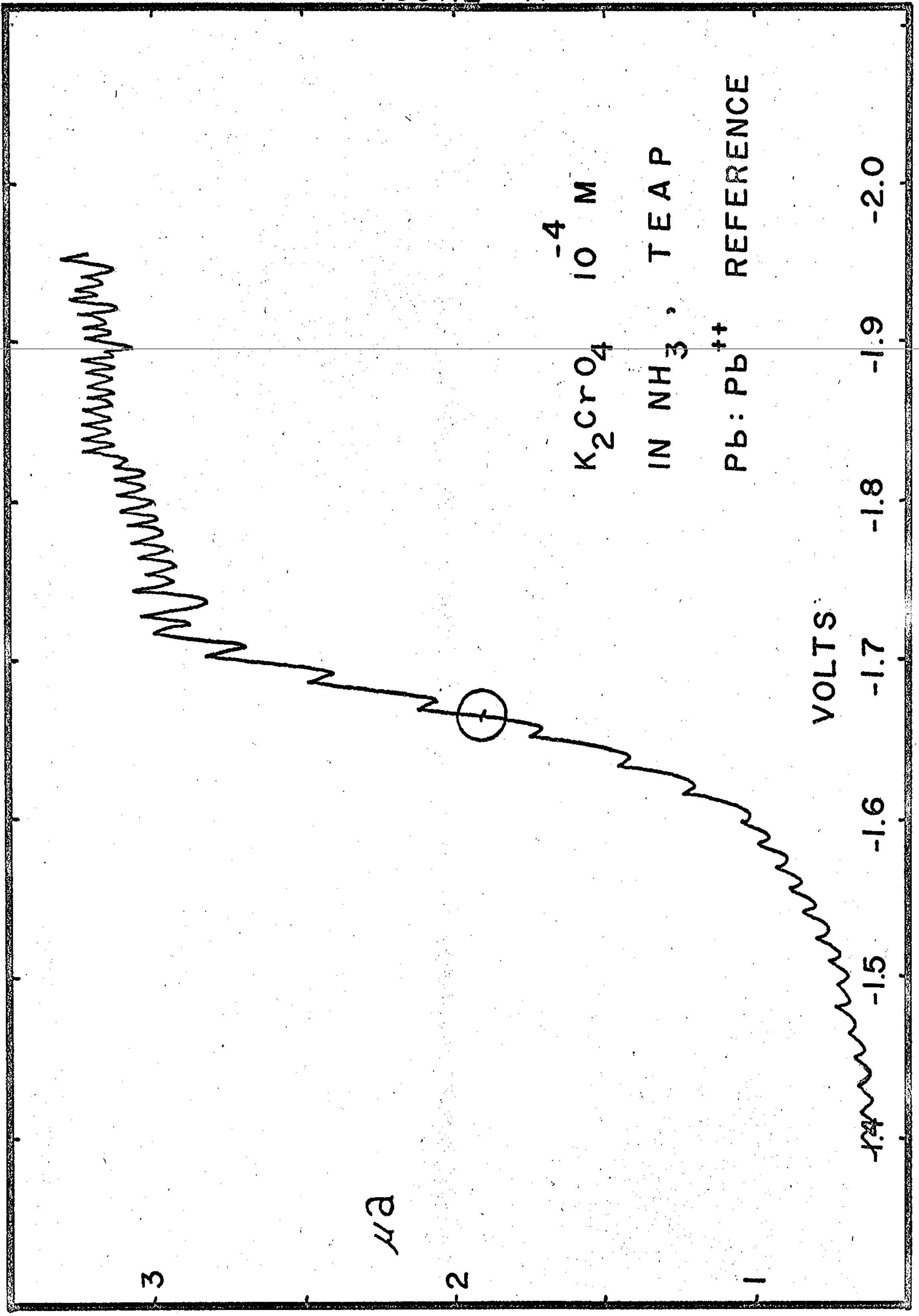

K_2CrO_4 10^{-4} M
IN NH_3, TEAP
Pb : Pb^{++} REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
1
2
3

FIGURE A - 25

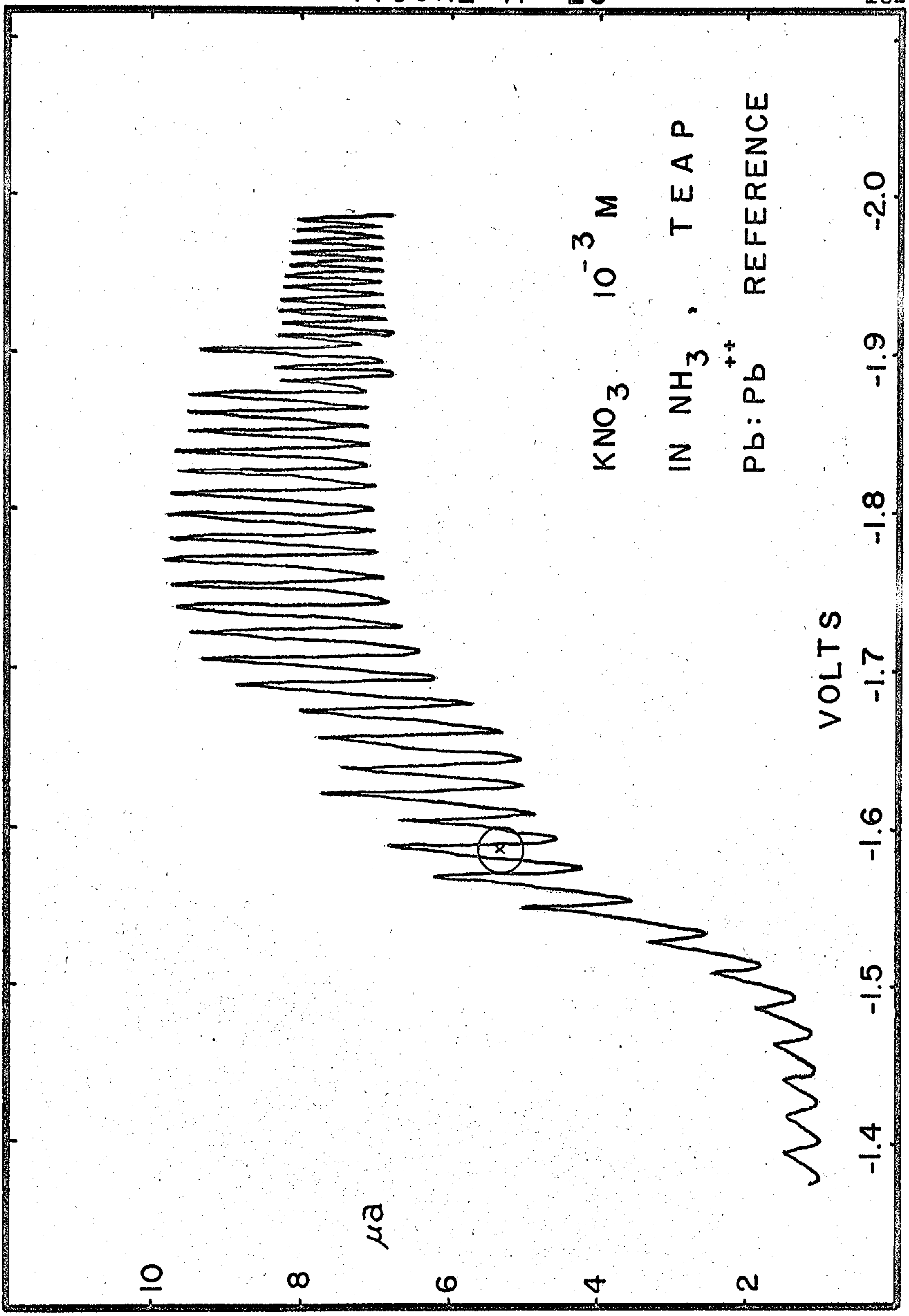

KNO_3 10^{-3} M
IN NH_3, TEAP
Pb:Pb^{++} REFERENCE
μa
10
8
6
4
2
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
VOLTS

FIGURE A - 26

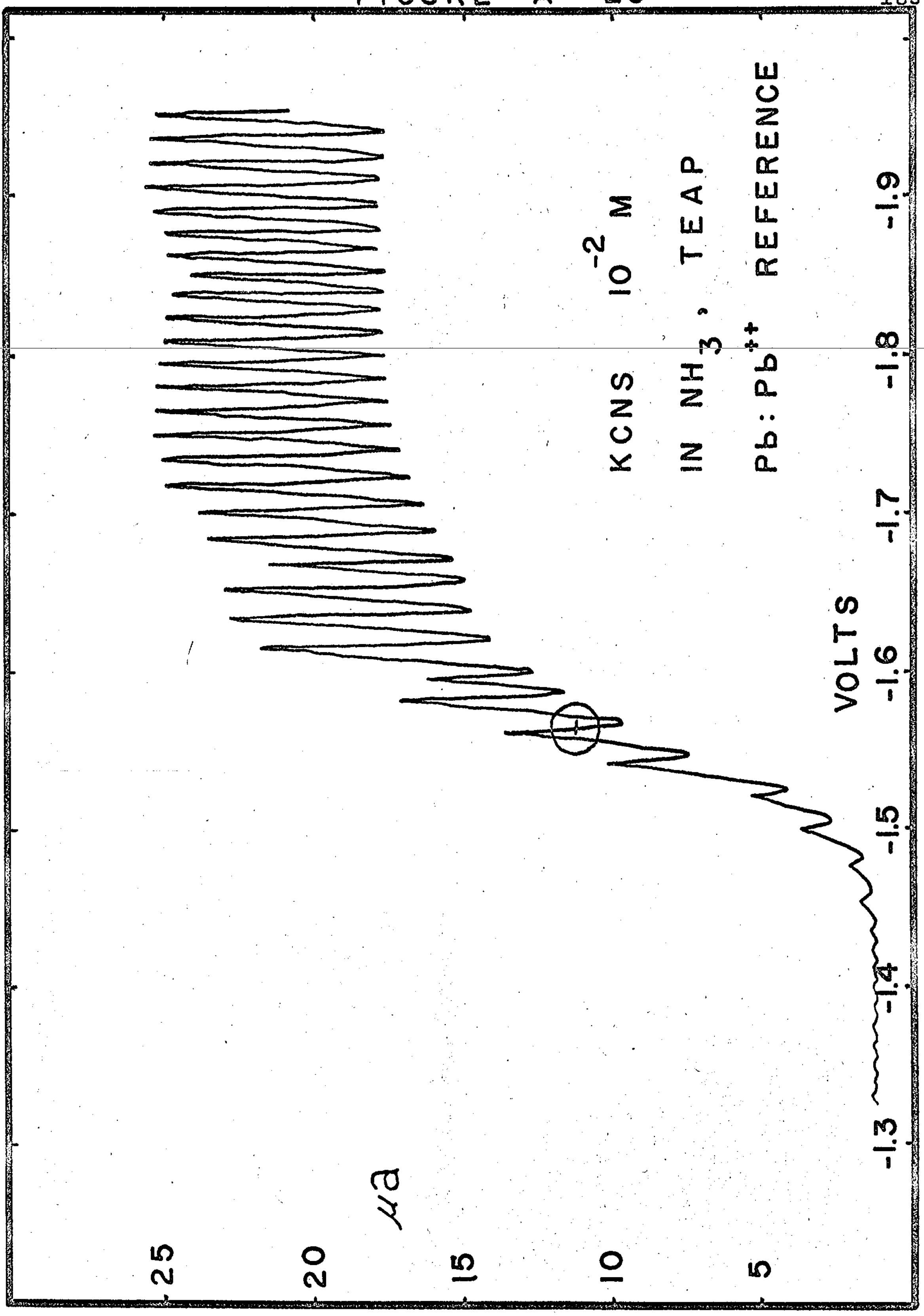

KCNS 10^{-2} M
IN NH_3, TEAP
Pb : Pb^{++} REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
μa
25
20
15
10
5

FIGURE A-27

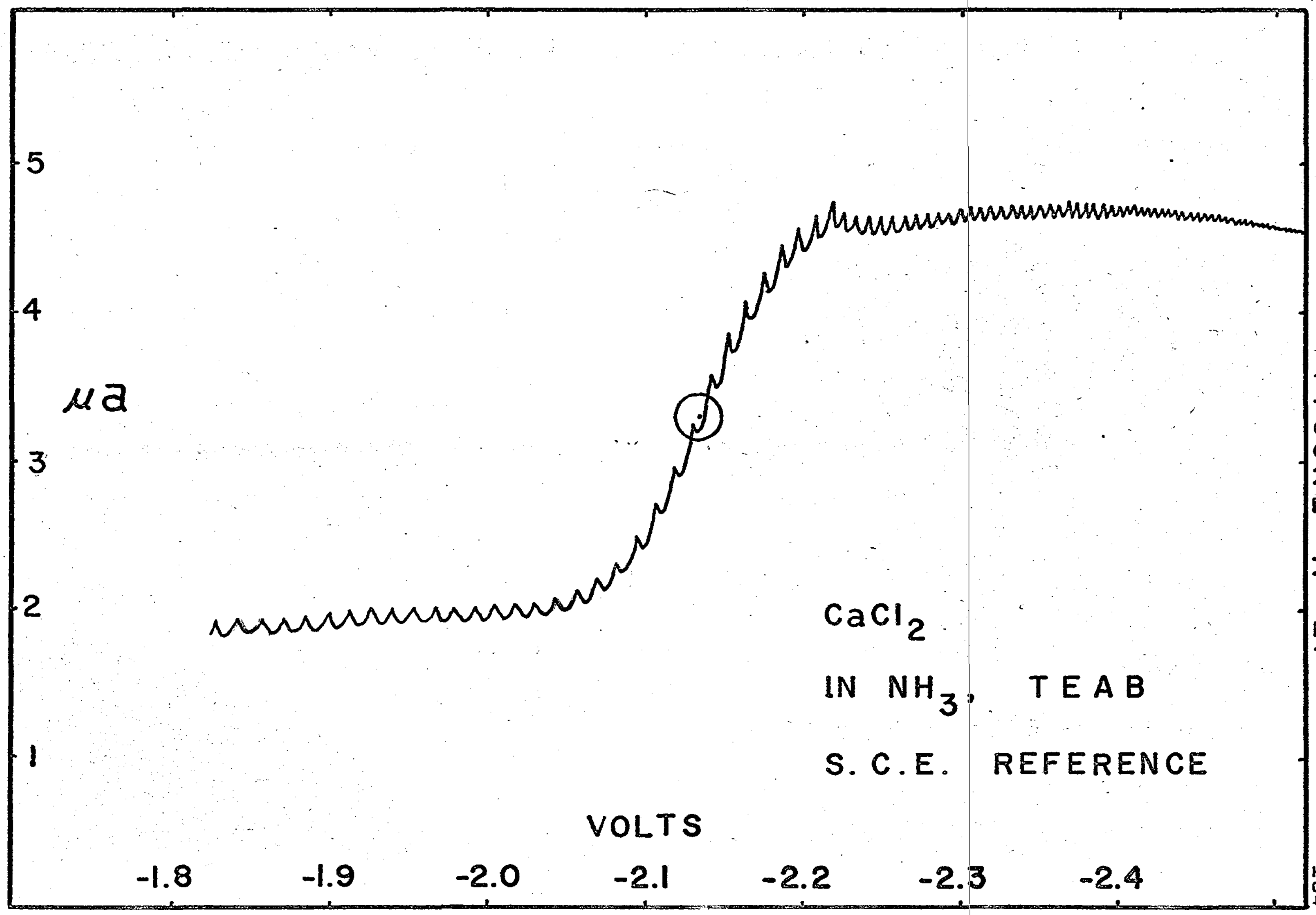

μa
5
4
3
2
1
CaCl₂
IN NH₃, TEAB
S. C. E. REFERENCE
VOLTS
-1.8
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4

FIGURE A-28

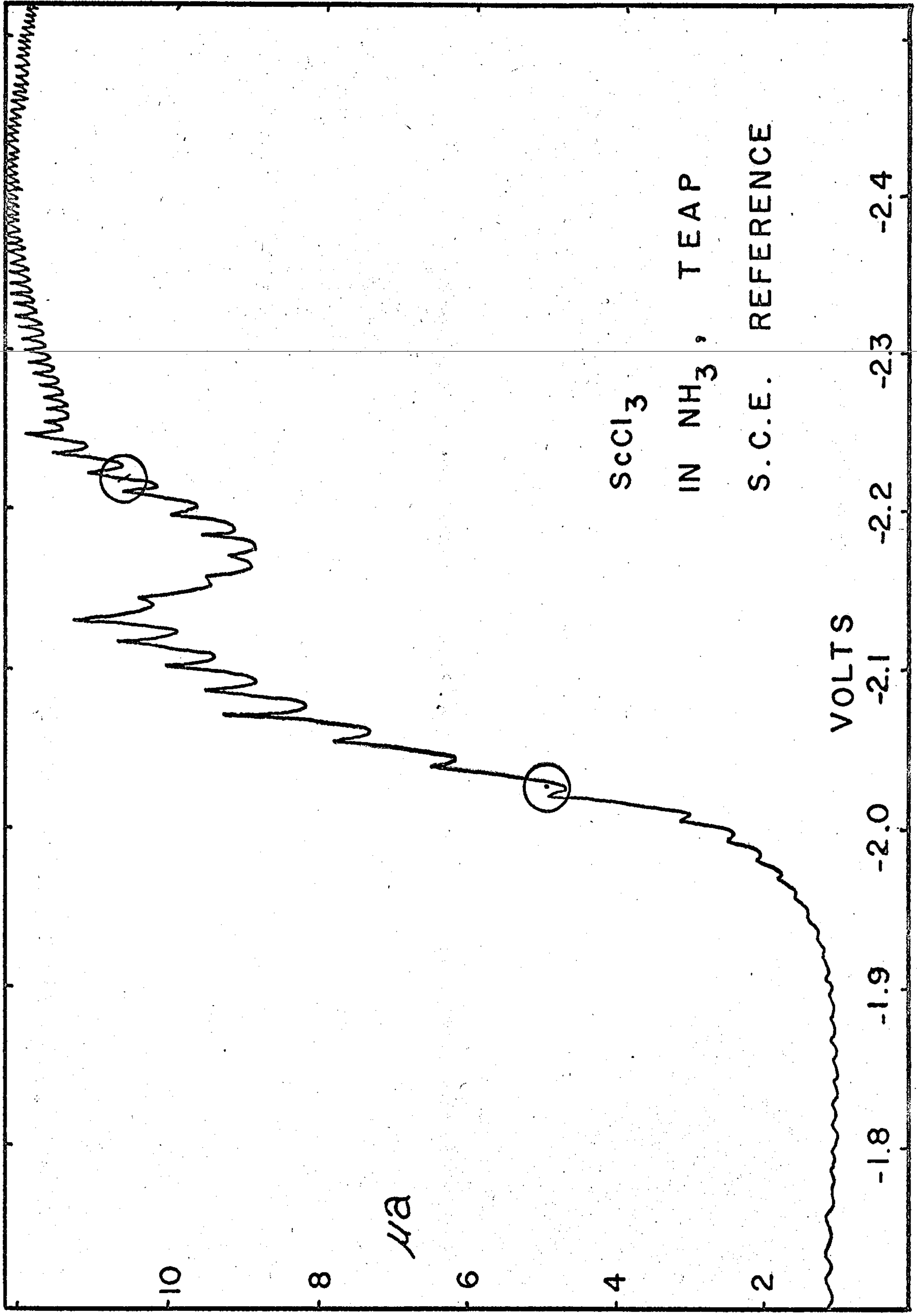
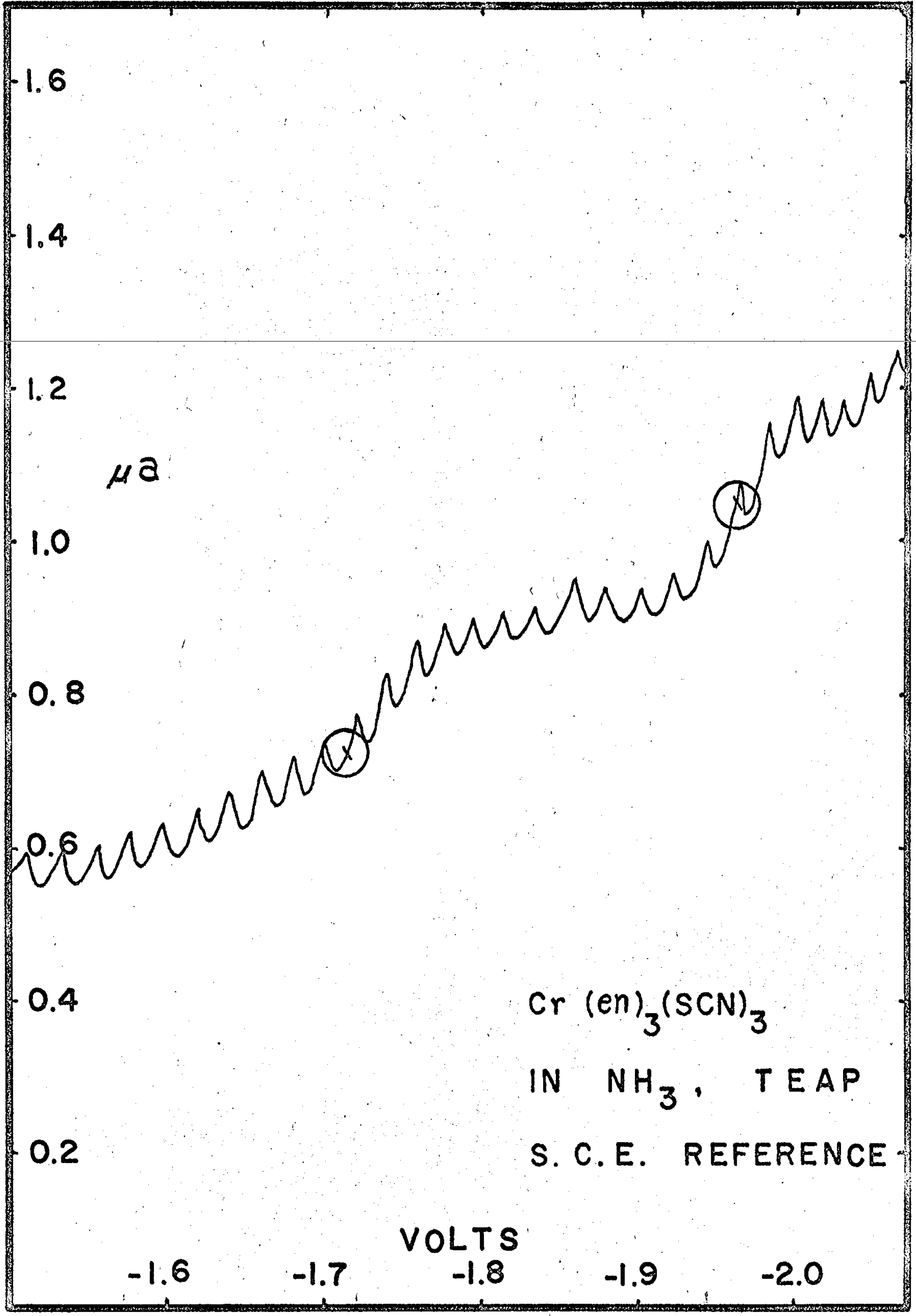

$ScCl_3$
IN NH_3, TEAP
S.C.E. REFERENCE
μa
10
8
6
4
2
VOLTS
-1.8
-1.9
-2.0
-2.1
-2.2
-2.3
-2.4

FIGURE A - 29


1.6
1.4
1.2
μa
1.0
0.8
0.6
0.4
0.2
Cr (en)$_3$(SCN)$_3$
IN NH$_3$, TEAP
S.C.E. REFERENCE
VOLTS
-1.6
-1.7
-1.8
-1.9
-2.0

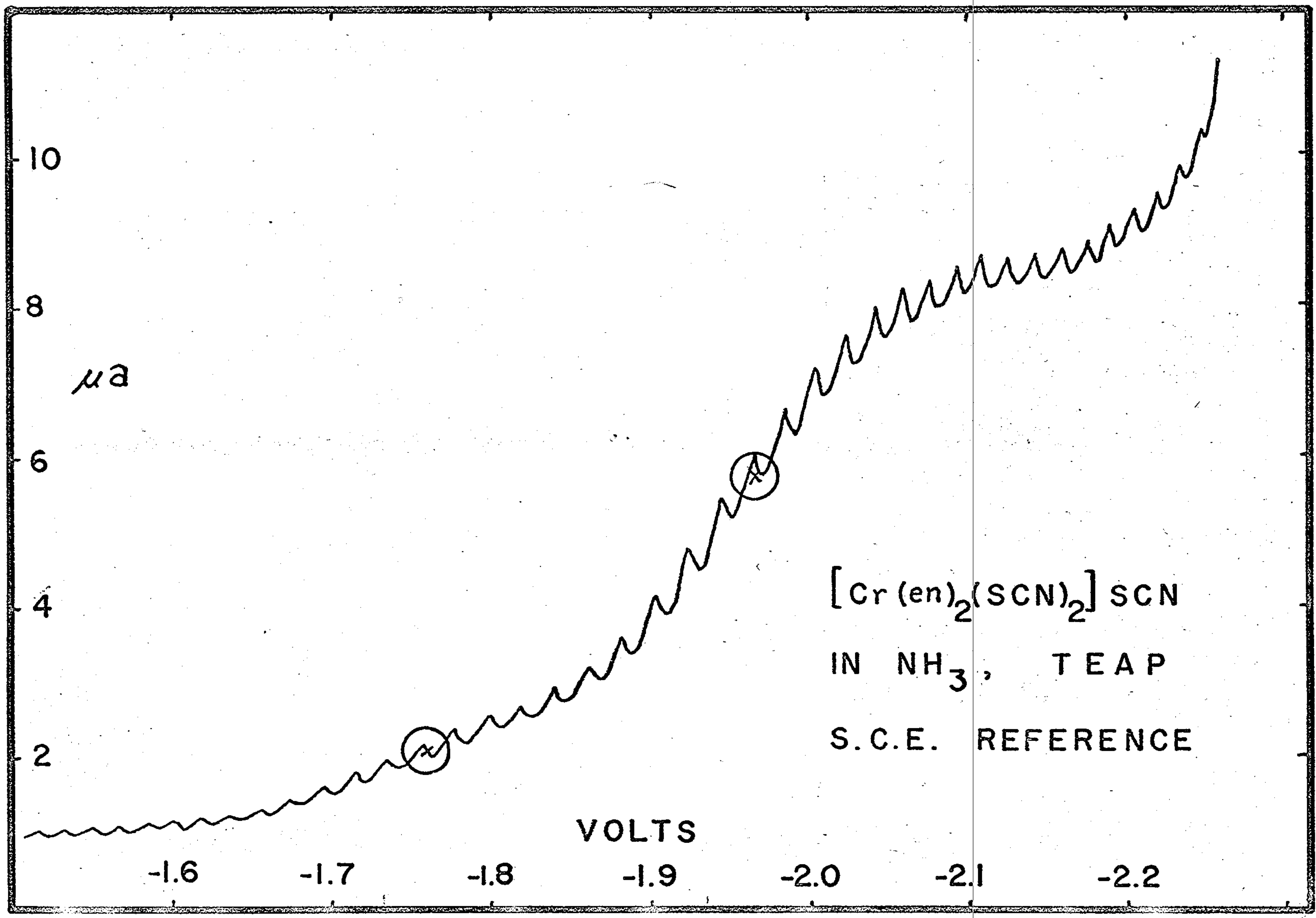

μa
10
8
6
4
2
VOLTS
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
[Cr(en)₂(SCN)₂] SCN
IN NH₃, TEAP
S.C.E. REFERENCE

FIGURE A-30

FIGURE A-31

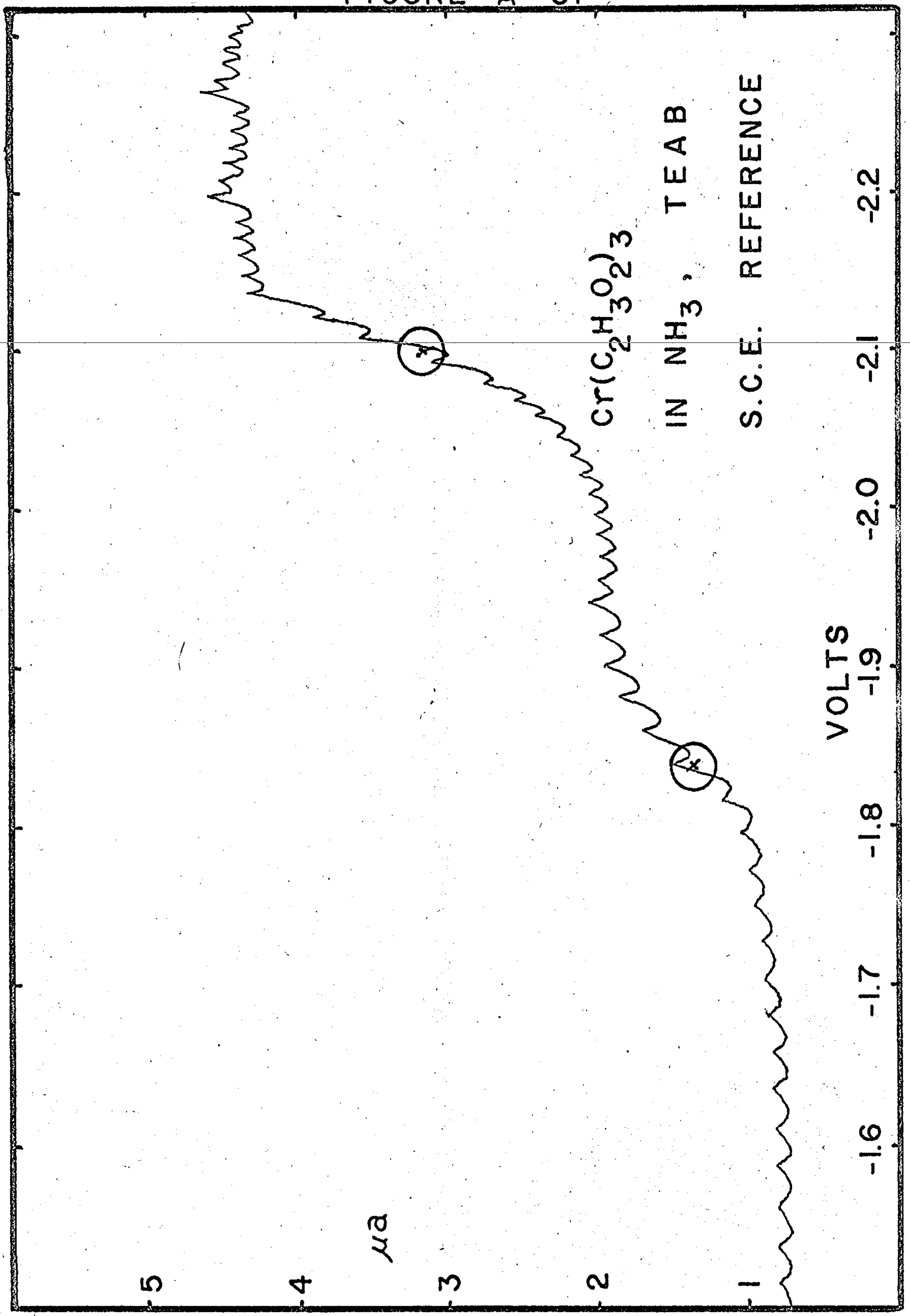

$Cr(C_2H_3O_2)_3$
IN NH_3, TEAB
S.C.E. REFERENCE
VOLTS
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
µa
1
2
3
4
5

FIGURE A - 32

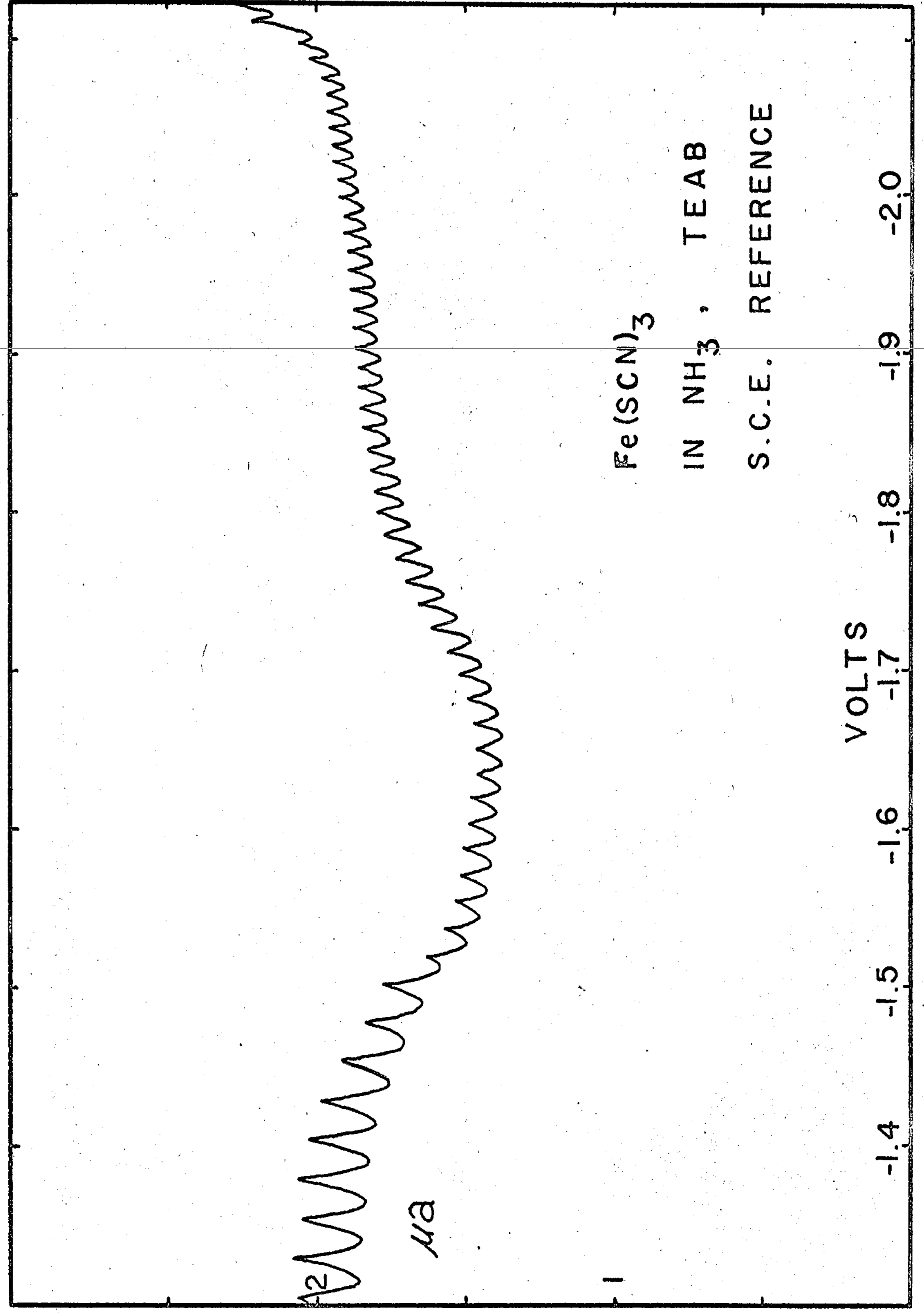

Fe(SCN)$_3$
IN NH$_3$, TEAB
S.C.E. REFERENCE
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0
μa
2
1

FIGURE A-33

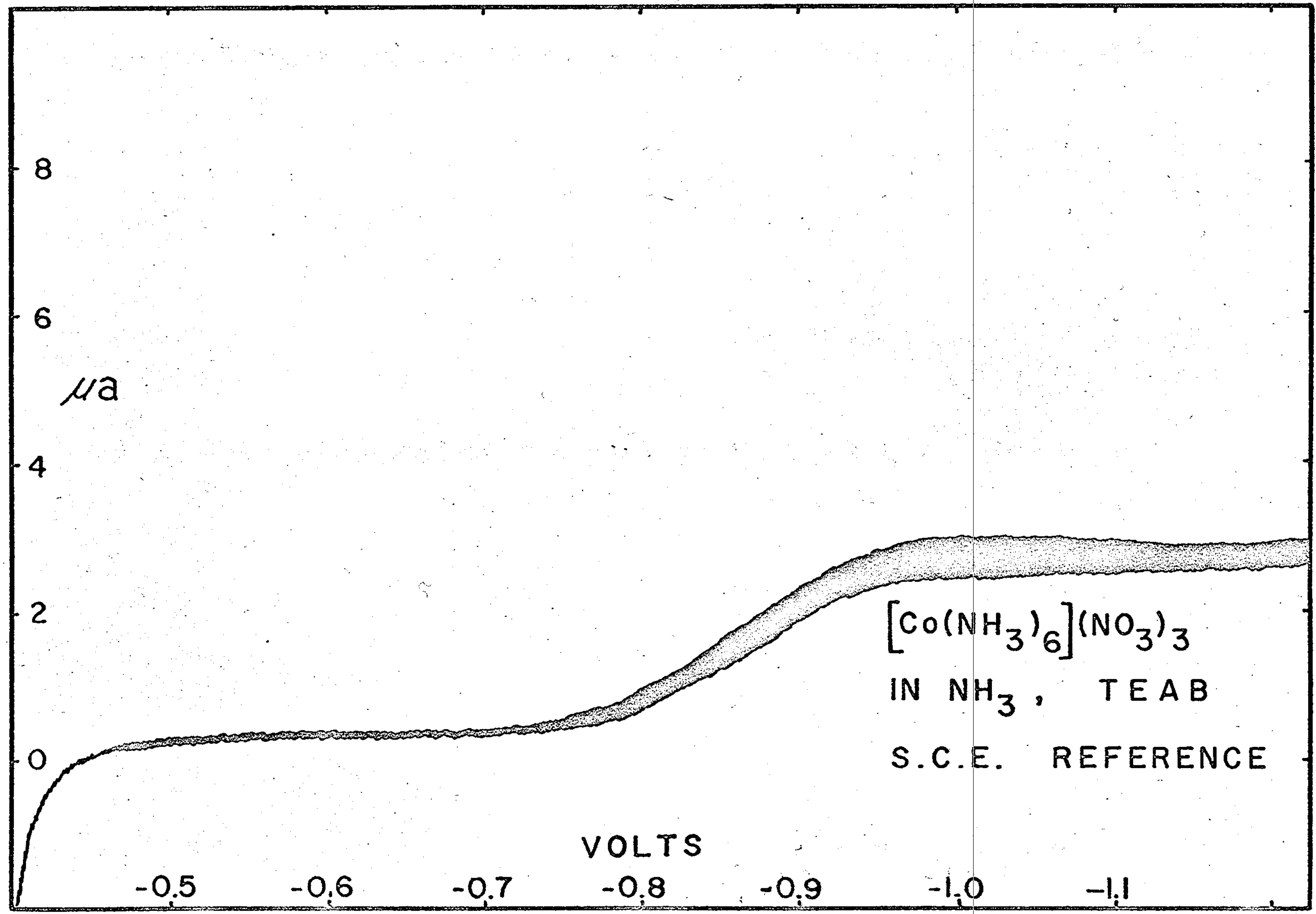

8
6
μa
4
2
0
VOLTS
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
$[Co(NH_3)_6](NO_3)_3$
IN NH_3, TEAB
S.C.E. REFERENCE

FIGURE A - 34

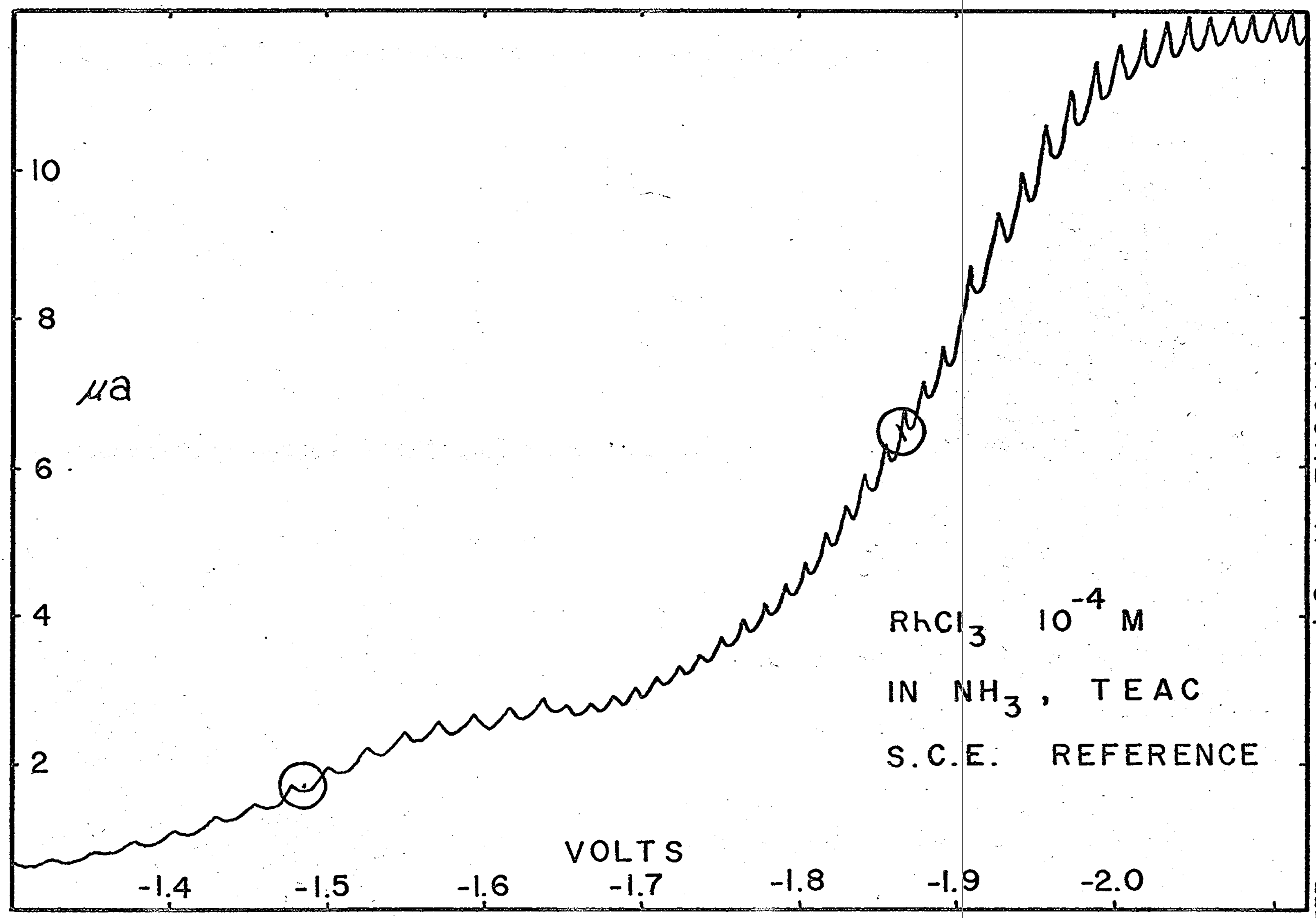

RhCl$_3$ 10^{-4} M
IN NH$_3$, TEAC
S.C.E. REFERENCE
μa
10
8
6
4
2
VOLTS
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2.0

FIGURE A-35

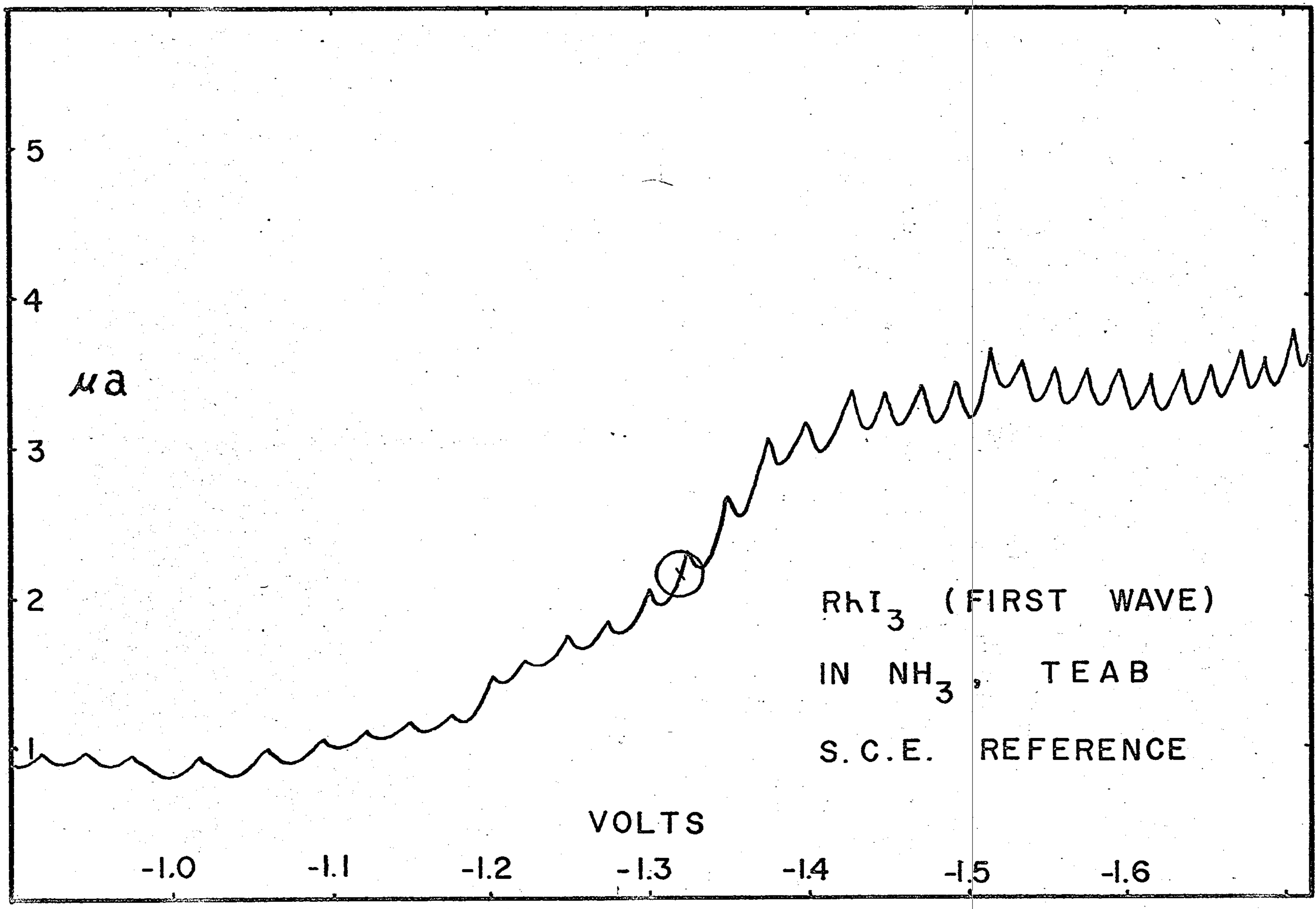
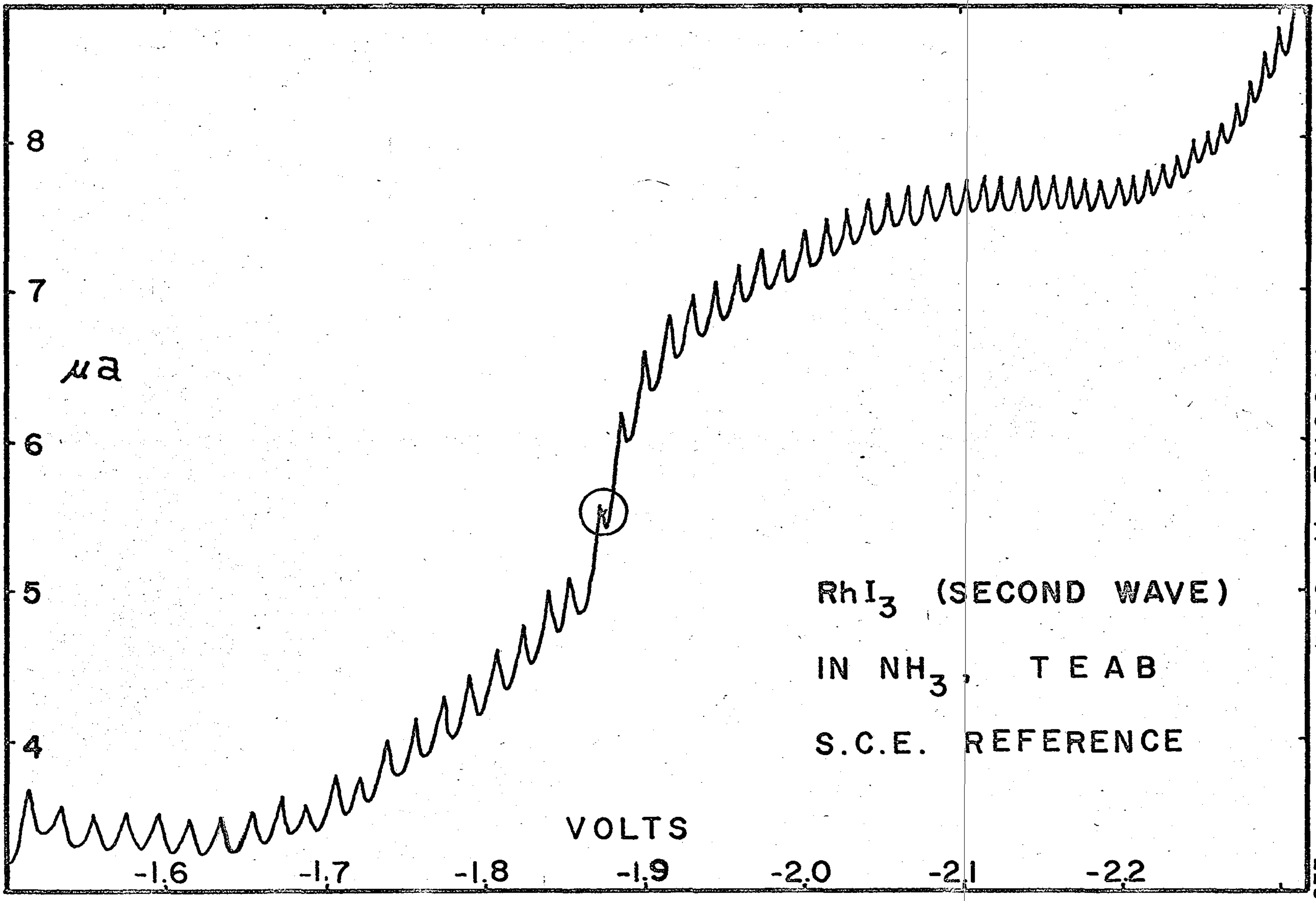

μa
5
4
3
2
1
RhI3 (FIRST WAVE)
IN NH3, TEAB
S.C.E. REFERENCE
VOLTS
-1.0
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6

FIGURE A-35a



μa
8
7
6
5
4
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
VOLTS
RhI_3 (SECOND WAVE)
IN NH_3, TEAB
S.C.E. REFERENCE

FIGURE A - 36

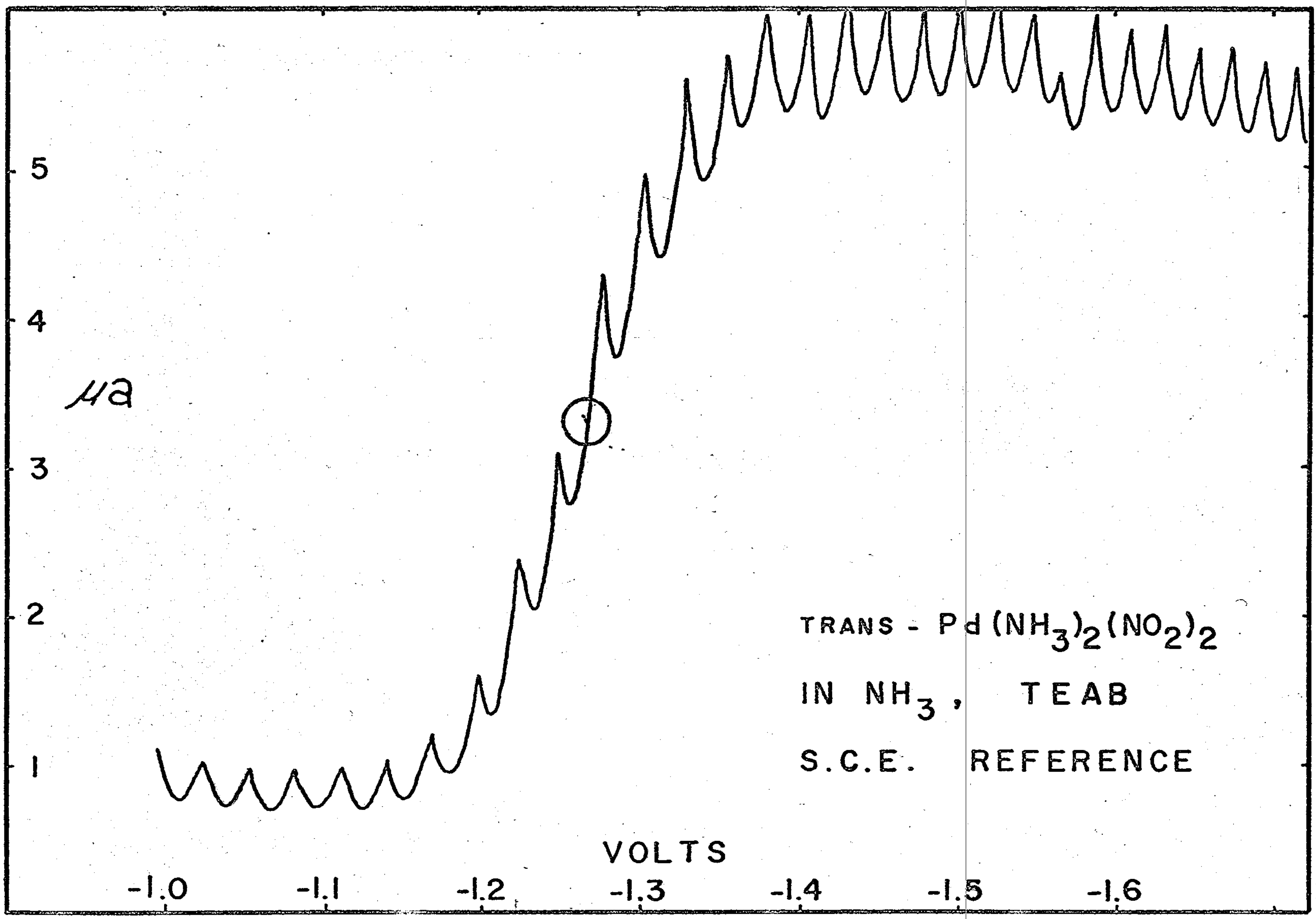

TRANS - Pd$(NH_3)_2(NO_2)_2$
IN NH_3, TEAB
S.C.E. REFERENCE
μa
1
2
3
4
5
VOLTS
-1.0
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6

FIGURE A-37

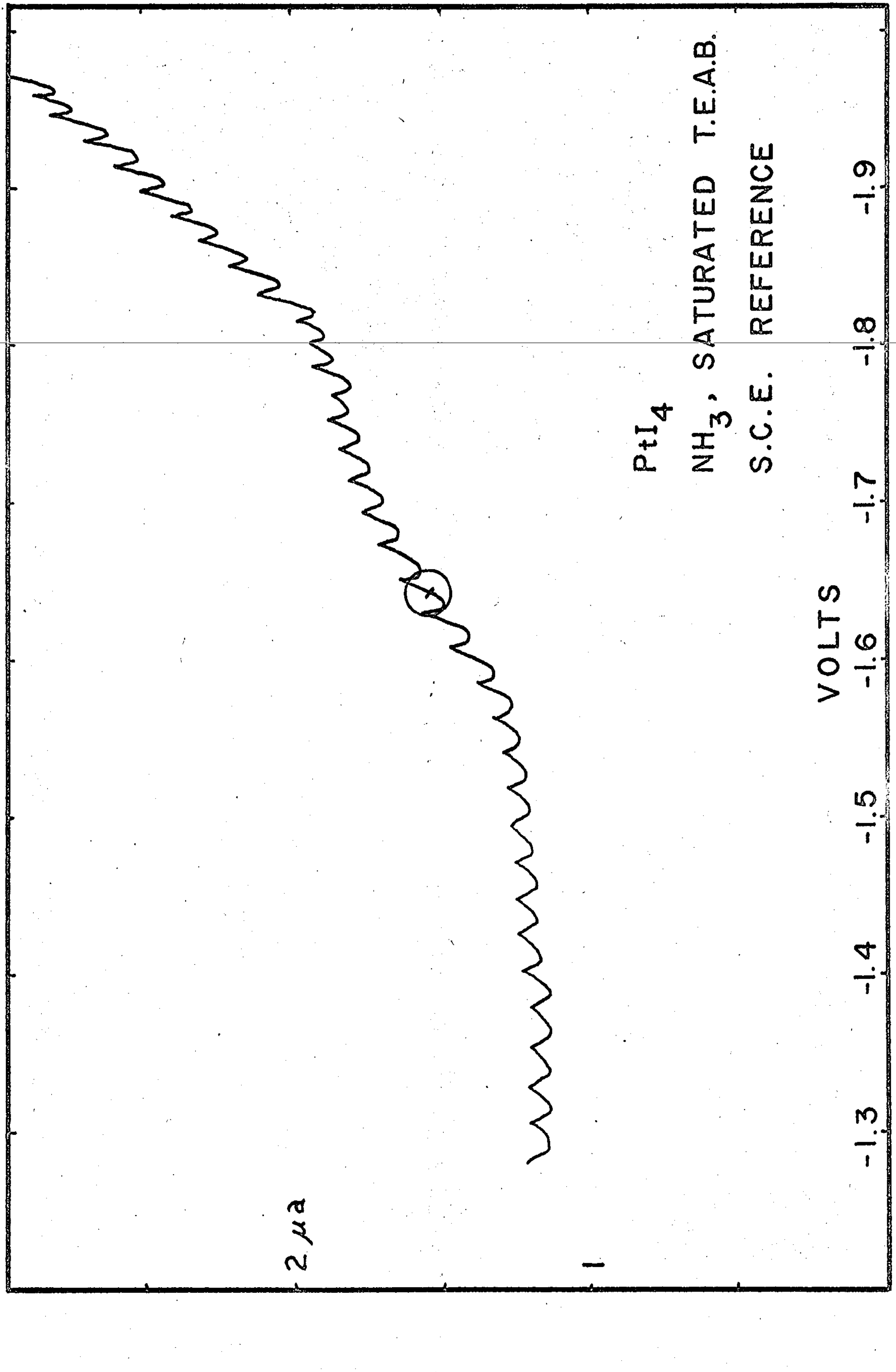

PtI_4
NH_3, SATURATED T.E.A.B.
S.C.E. REFERENCE
VOLTS
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
2 μa

FIGURE A - 38

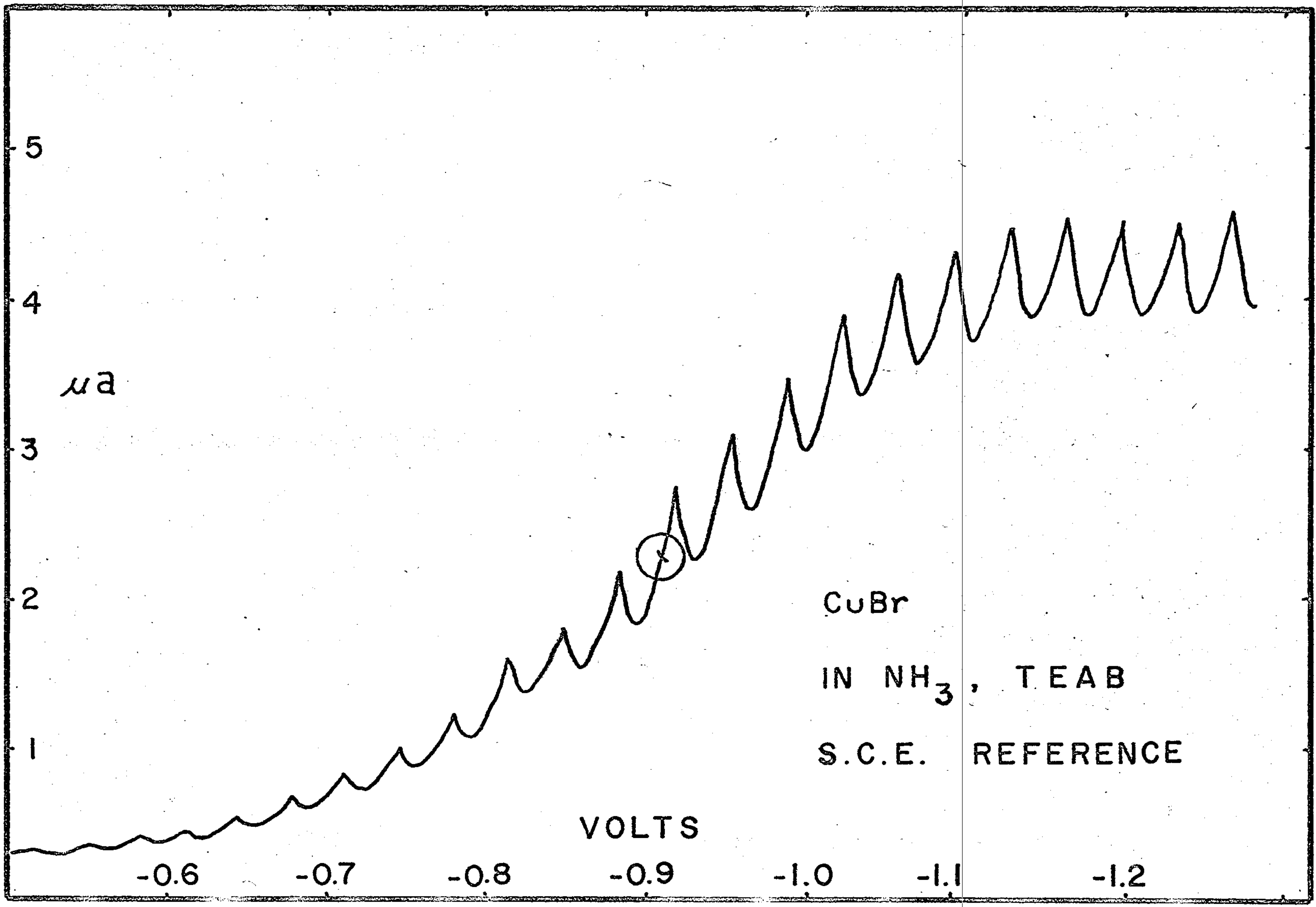

5
4
3
2
1
μa
CuBr
IN NH_3, TEAB
S.C.E. REFERENCE
VOLTS
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2

FIGURE A - 39

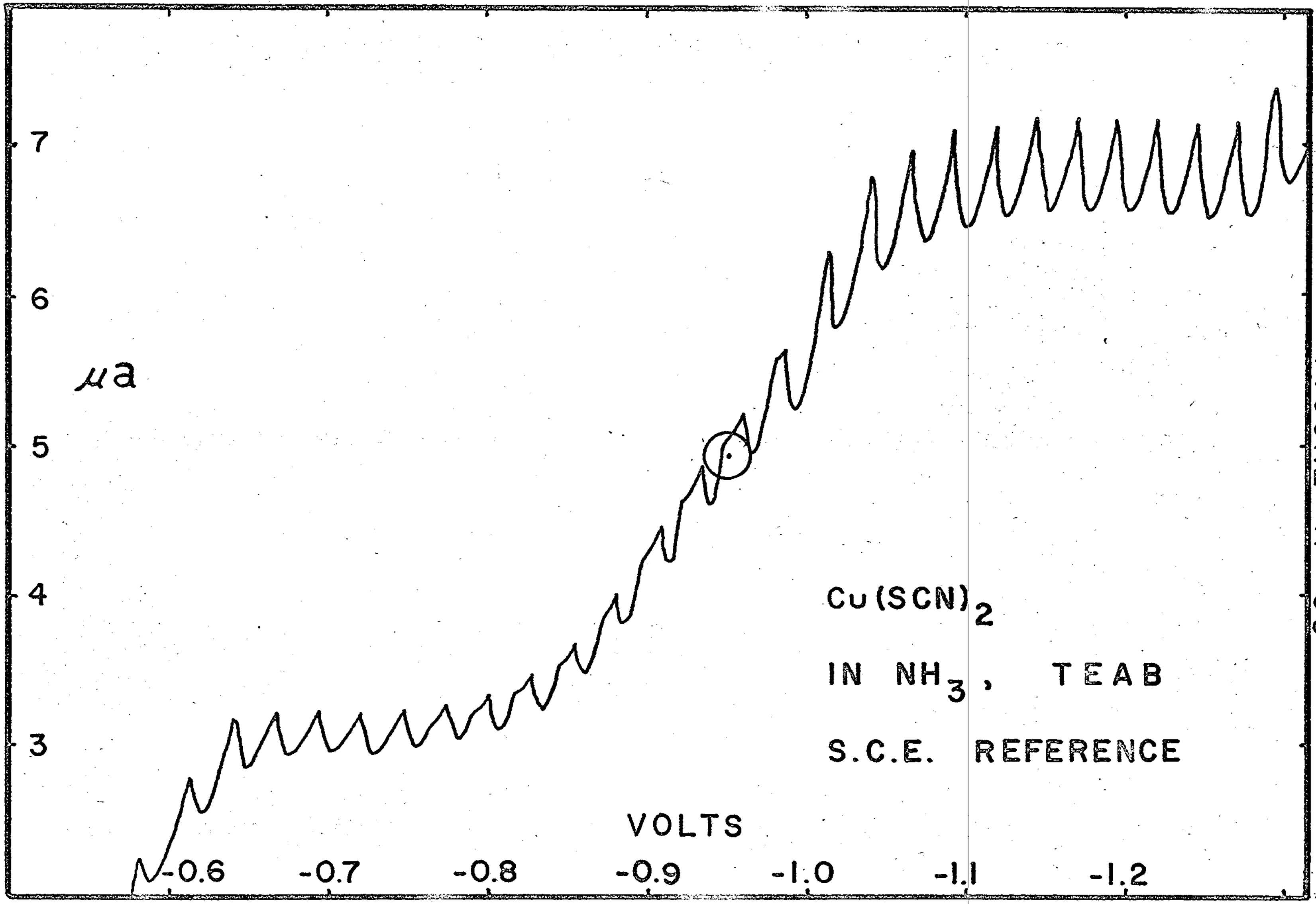

μa
7
6
5
4
3
VOLTS
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
Cu(SCN)$_2$
IN NH$_3$, TEAB
S.C.E. REFERENCE

FIGURE A - 40

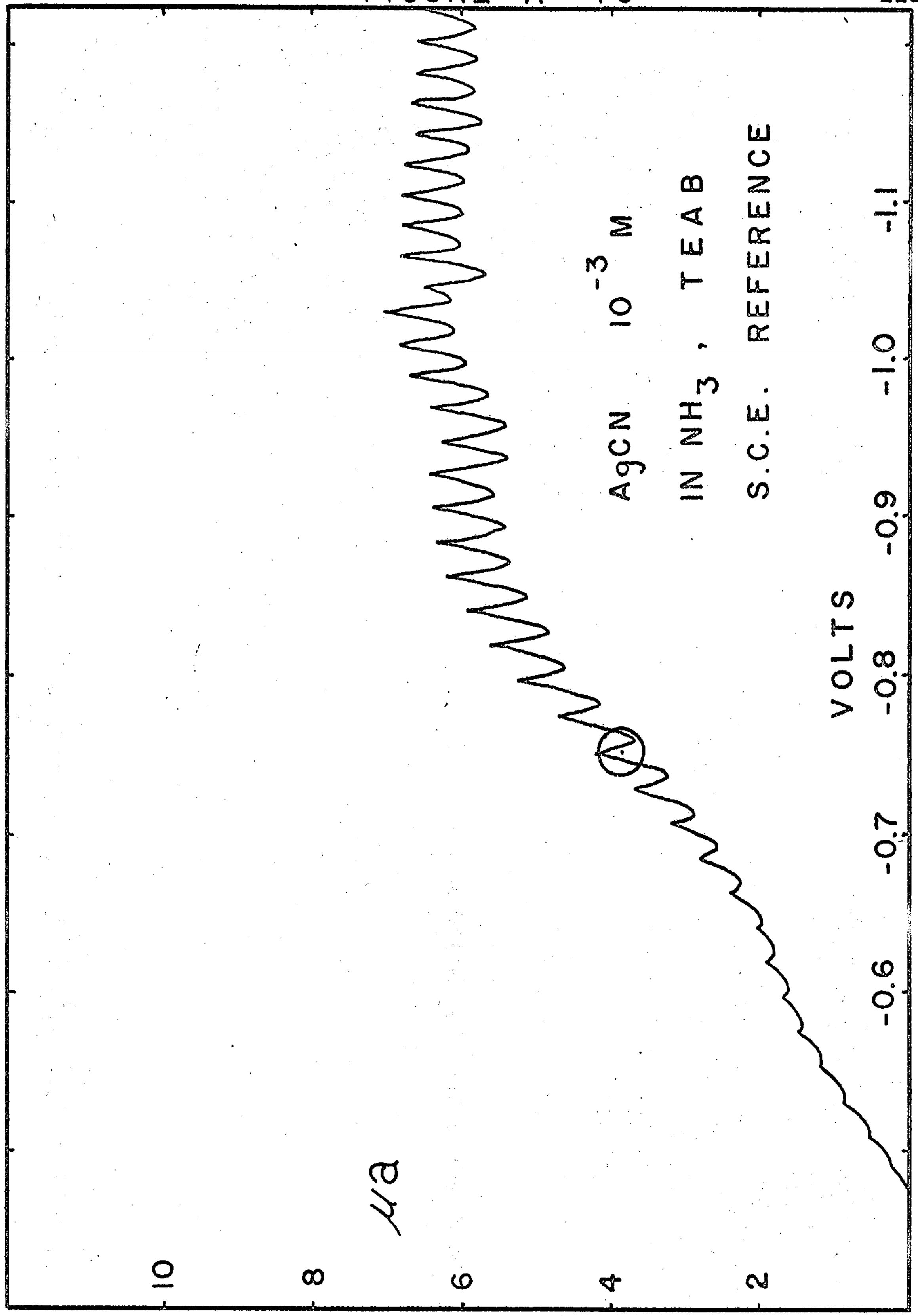

AgCN 10^{-3} M
IN NH_3 , TEAB
S.C.E. REFERENCE
VOLTS
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
μa
10
8
6
4
2

FIGURE A - 40a

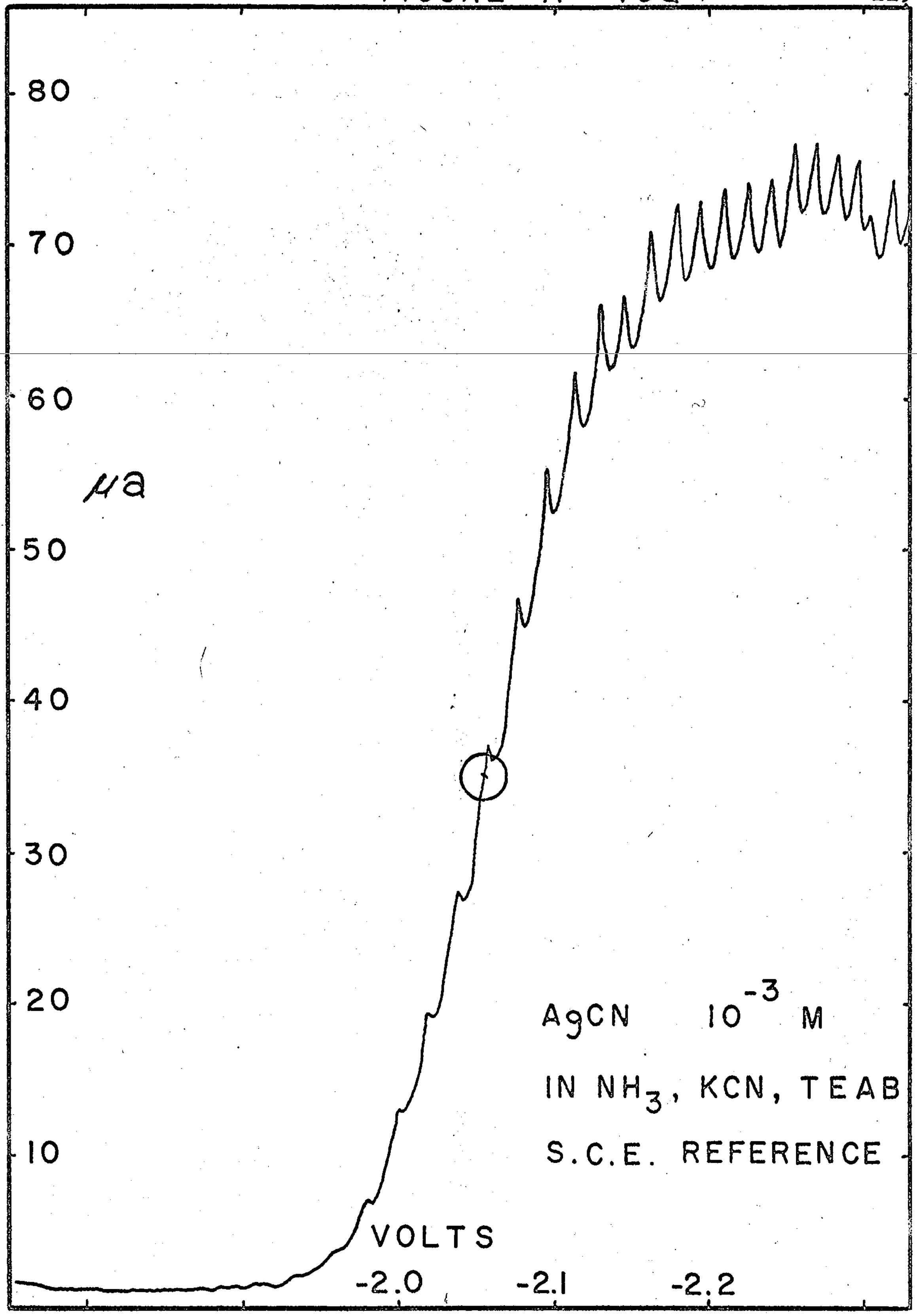

80
70
60
μa
50
40
30
20
10
AgCN 10^{-3} M
IN NH_3, KCN, TEAB
S.C.E. REFERENCE
VOLTS
-2.0
-2.1
-2.2

FIGURE A-41

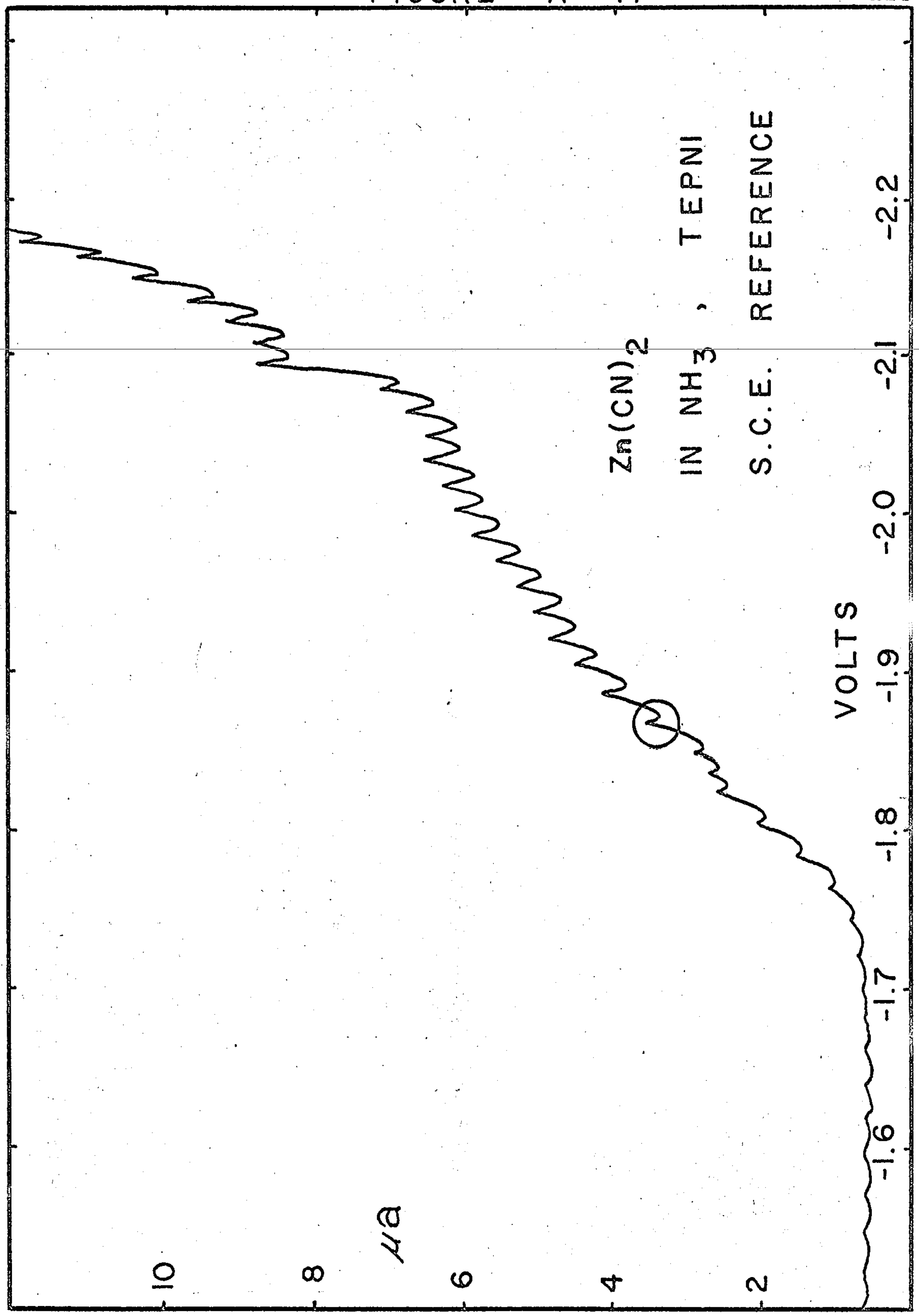

Zn(CN)$_2$
IN NH$_3$, TEPNI
S.C.E. REFERENCE
VOLTS
-1.6
-1.7
-1.8
-1.9
-2.0
-2.1
-2.2
μa
2
4
6
8
10

FIGURE A - 42

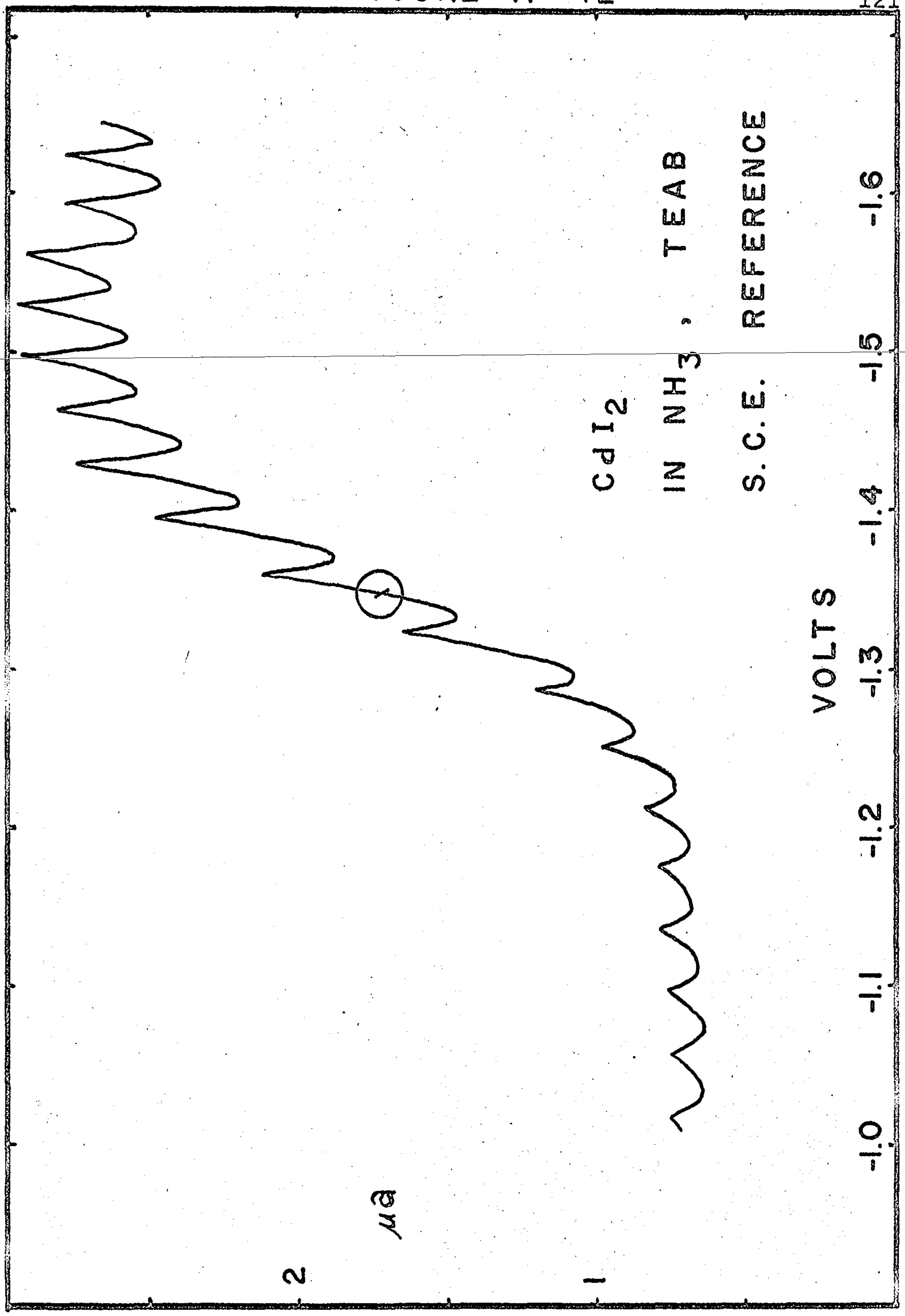


FIGURE A - 43

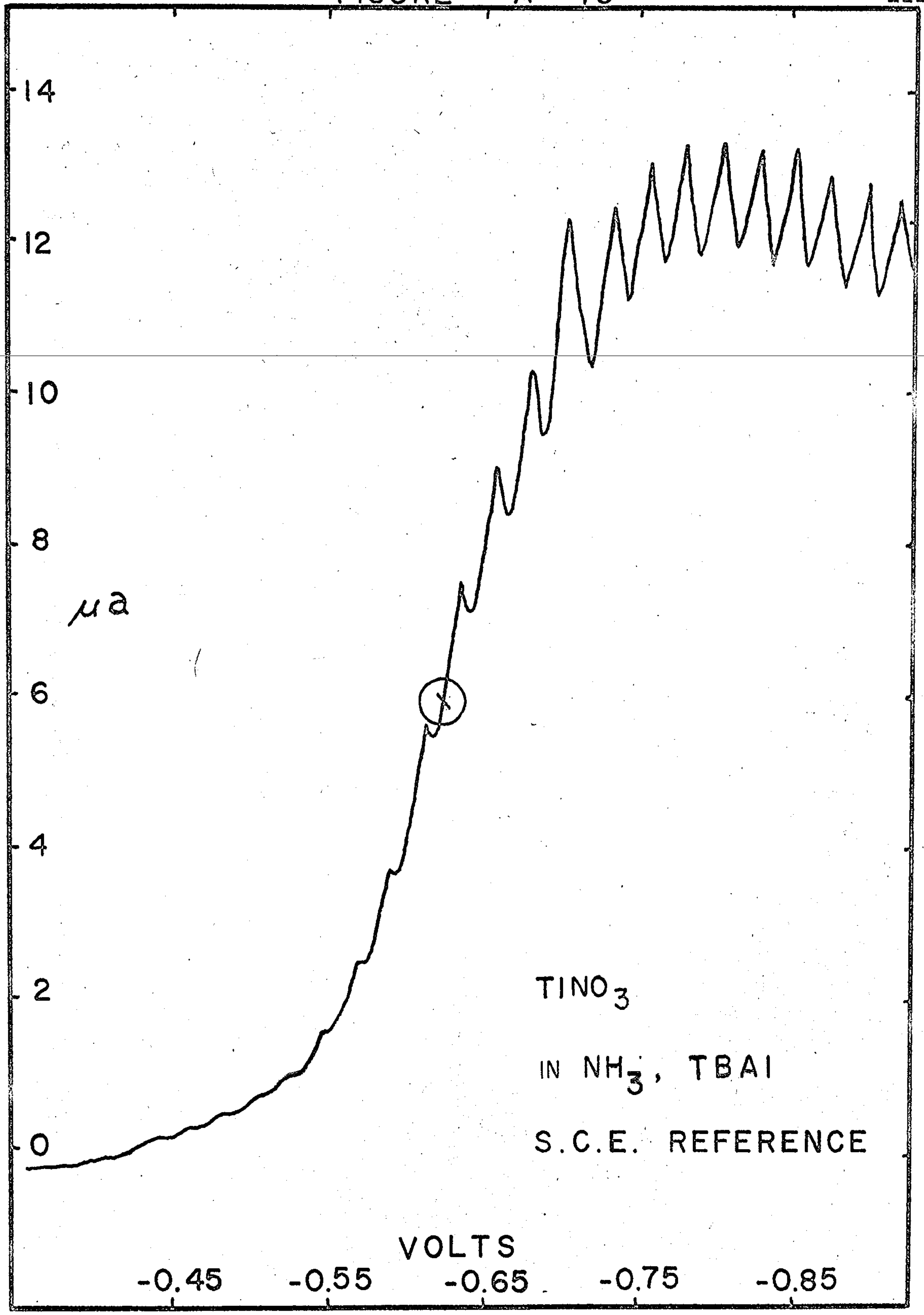

14
12
10
8
μa
6
4
2
0
$TlNO_3$
IN NH_3, TBAI
S.C.E. REFERENCE
VOLTS
-0.45
-0.55
-0.65
-0.75
-0.85

FIGURE A - 44

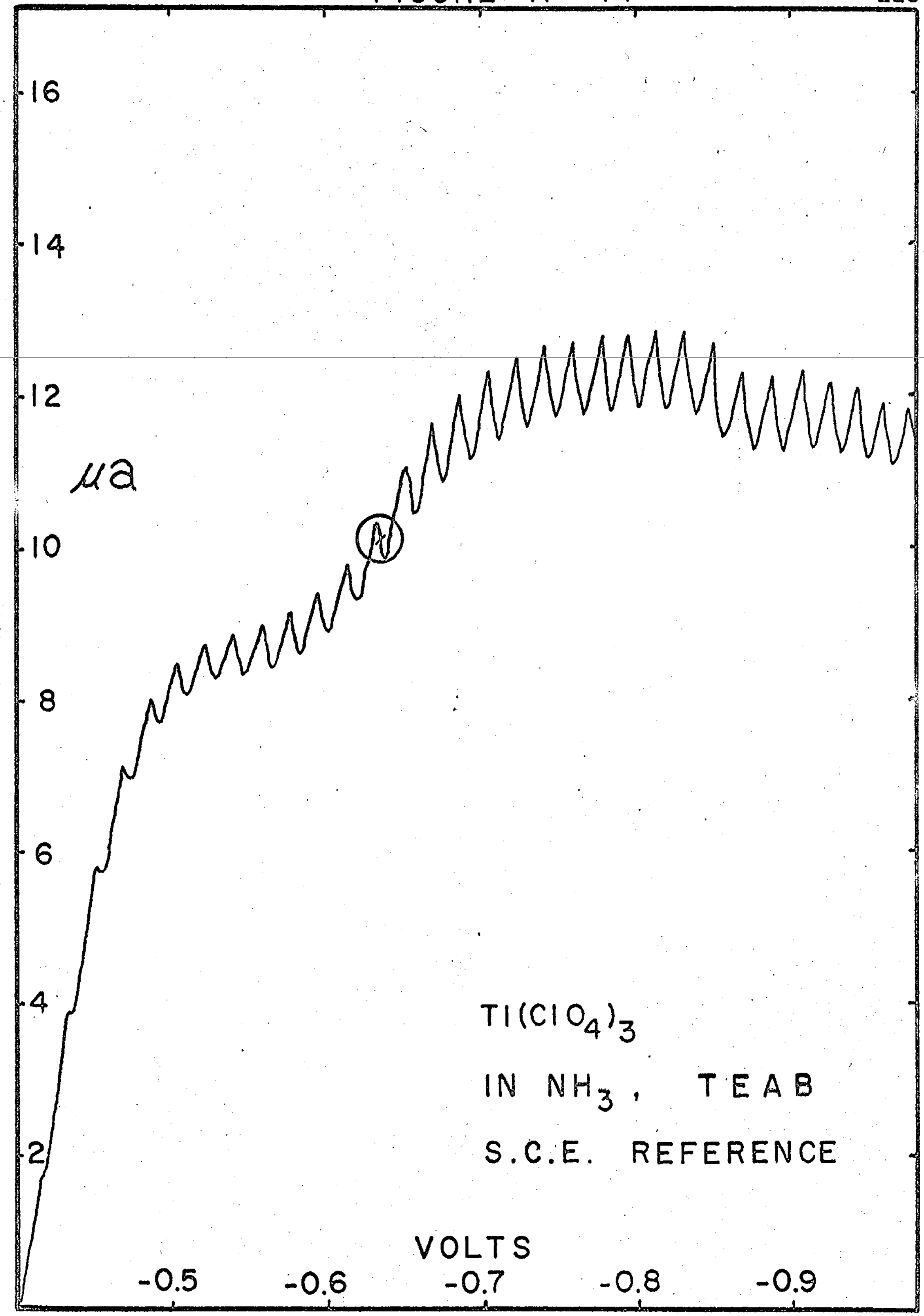
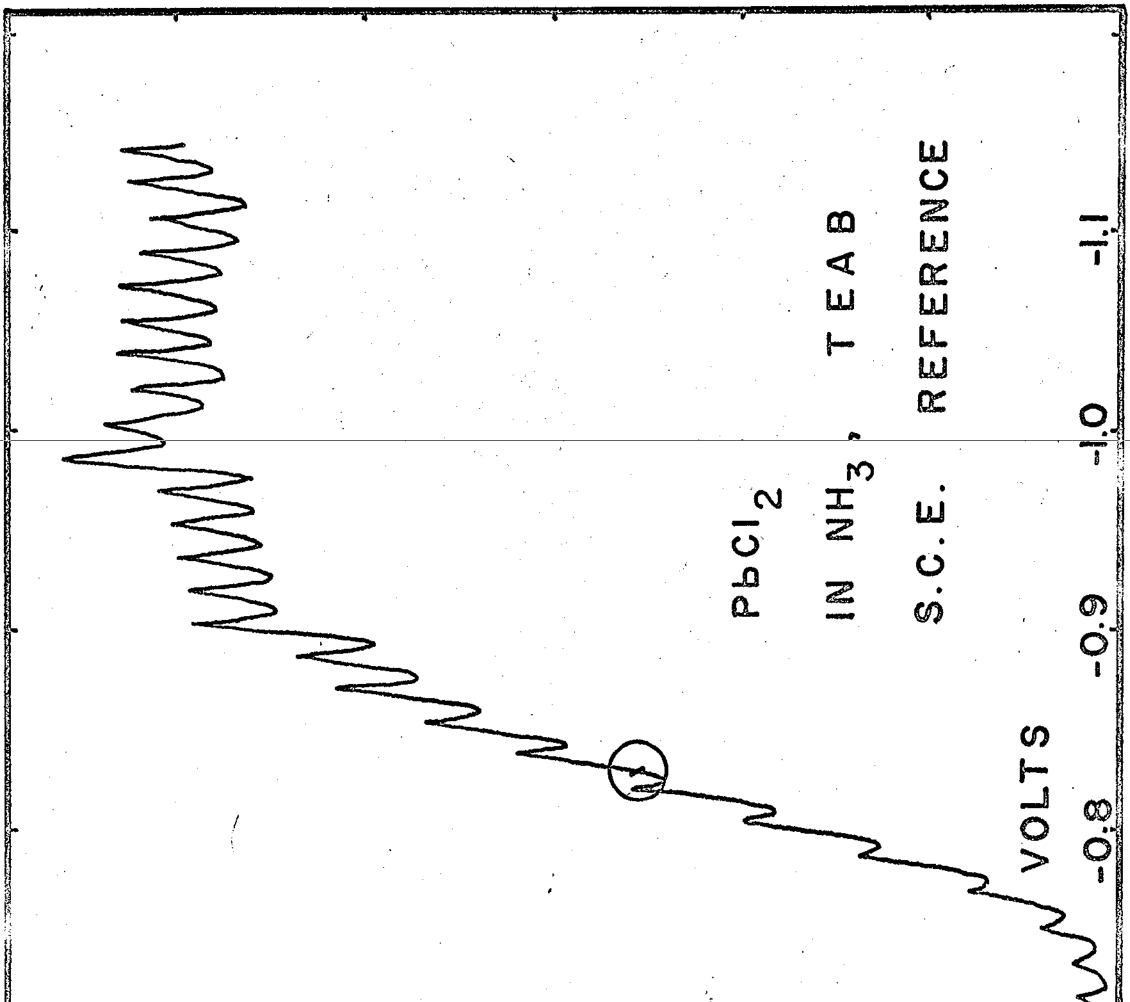

16
14
12
10
8
6
4
2
μa
VOLTS
-0.5
-0.6
-0.7
-0.8
-0.9
$Tl(ClO_4)_3$
IN NH_3, TEAB
S.C.E. REFERENCE

FIGURE A - 45



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