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Tellurium (VI): Polarography and polyol complexes

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TELLURIUM (VI): POLAROGRAPHY AND POLYOL COMPLEXES

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Peter T. Kissinger

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Bachelor of Science with a Major in Chemistry

is approved by

"The chymists are a strange class of mortals
impelled by an almost insane impulse to seek
their pleasure among smoke and vapour, soot
and flame, poisons and poverty; yet among
all these evils I seem to live so sweetly,
that I may I die if I would change places with
the Persian King." (1)

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HISTORICAL BACKGROUND

AND

GENERAL INTRODUCTION

In 1782 the element tellurium was discovered by
Baron Franz Joseph Müller von Reichenstein. Müller first
isolated the element from Transylvanian gold ore (2).
Klaproth verified this work and in 1798 proposed that the
substance be called tellurium. The etymology of the word
begins with the Latin noun tellus, meaning earth.
Students of Roman mythology will recall the ancient deity,
Tellus, goddess of marriage and fertility. The history of
the discovery of tellurium is a particularly interesting
one. Serious students of the element will enjoy reading
the account given by Mary Eliva Weeks (3,4,5).

The properties of tellurium are consistent with its
position in the periodic table as element number 52. The
elements of Group VI include the non-metals oxygen and
sulphur, the semiconductors selenium and tellurium, and
the radioactive metal polonium. Selenium and tellurium
are closely related in many ways and they are often
discussed conjointly.

In aqueous solutions the most common oxidation states for tellurium are -2, 4, and 6. In the plus six state the element is usually encountered as telluric acid, H_6TeO_6. When the element or its oxide TeO_2 is subjected to strong oxidizing agents, telluric acid is formed.

The electronic configuration for the native element $[Kr] 4d^{10}5s^25p^4$ permits d^2sp^3 hybridization for the hexavalent atom and explains the diamagnetic octahedral configuration of the acid, $Te(OH)_6$. This octahedrally symmetrical structure was experimentally confirmed by Pauling (6).

Telluric acid is a weak dibasic acid, the first and second ionization constants being reported as 2.00×10^{-8} and 9.2×10^{-12} respectively (7). It is a fairly strong oxidizing agent and tends to polymerize in solution. A three-dimensional network may be formed by hydrogen bonding. An important consideration is that telluric acid is not analogous to the other nexavalent group six acids, namely, sulphuric (H_2SO_4) and selenic (H_2SeO_4) acids. The later two, unlike telluric acid, contain nonhydroxylic oxygen atoms and are thus much stronger acids.

POLYOL COMPLEXES

That polyhydroxy alcohols and oxyanions form complex ions has been established for some years. Complexation of this sort has been observed since at least as early as 1842 when Biot (8) noted that sugars enhanced the acidity of boric acid solutions. This characteristic of enhanced acidity is due to the fact that the complexation effectively pulls the anions out of the ionization reaction, thus forcing more of the neutral acid to dissociate. In addition to boric acid, polyol complexes have been studied for phenylboric, germanic, arsenious, periodic, and telluric acid .

The most important work in this area has been done by J.O. Edwards at Brown University and P.J. Antikainen at the University of Helsinki. Edwards _et al_ have published a number of papers in which polyol-tellurate complexes have been considered (9,10,11,12,13,14,15,16). Potentiometric, pH, and spectrophotometric methods were employed. Antikainen (17) has used potentiometric and cryoscopic procedures for similar studies.

Edwards has proposed the following general equation for simple glycol-orthotellurate complexation:

$$H_6TeO_6 \longrightarrow H_5TeO_6^- + H^+ \qquad (I)$$

$$+ \; 2HOH \qquad (II)$$
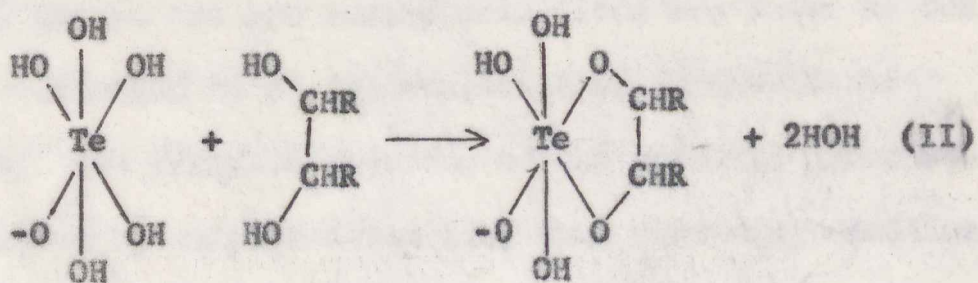
The formation constants were found to be large and only 1:1 complexes were considered extant. The driving force of the reaction is an entropy increase related to the formation of 3 products from 2 reactants (13). A five membered ring is favored by the 90 degree O-Te-O bond angle.

In later work Lanese (18) proposed a similar structure for the d-tartrate-orthotellurate complex.
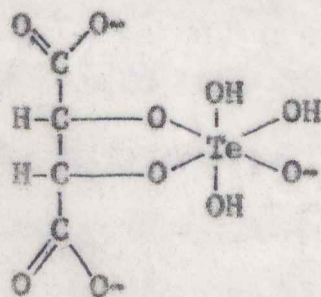
A thorough polarimetric study of this complex gave evidence for a one-to-one stoichiometry. Apparent stability constants were found to be 45 ± 2.5 at pH 9.5 and 62.0 ± 3.1 at pH 12. An analysis of the lithium salt of the complex

indicated that the charge on the species was -3. That the carbonyl groups are not susceptible sites was shown by the lack of variation in pH for complexation in unbuffered solution. The infrared spectrum of the carboxyl group was not affected by complex formation, thus providing additional evidence.
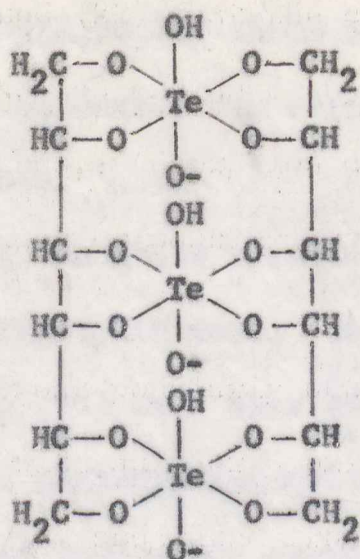
The tartrate complexation requires the removal of hydrogens from the hydroxyl groups. This should explain why the stability constants vary with pH (19). In addition, the relative participation of the species H_6TeO_6, $H_5TeO_6^-$, and $H_4TeO_6^=$ in a pH dependent way must be considered. It is understandable that the probability for the complex to form should decrease rapidly below a certain pH and become negligible in strongly acid solutions. Lanese gives a lower limit of pH 5 and concludes that the formation of the complex is dependent upon the existence of the tartrate ion $C_4H_4O_6^{-2}$ and independent of the orthotellurate species that may be present (20).

The fact that selenium (VI) and certain other oxyanions do not complex with tartrate would suggest a valuable analytical application. Lanese developed a polarimetric method based on the direct dependence of optical rotation on the addition of tellurate to solutions of d-tartrate (21).

It has been intimated (22) that the complex might be use-
fully employed in an ion exchange separation of tellurate
from similar oxyanions. Adsorption chromatography on an
alumina column is another possibility deserving considera-
tion.

Tellurium is most popularly determined gravimetri-
cally by reduction with sulphur dioxide in a hydrochloric
acid medium and may be separated from selenium by distill-
ation from a solution of mixed acids (23). Sulphur dioxide,
however, will only reduce Te(IV) whereas hydrazine will
reduce both the IV and VI oxidation states (24).

A more typical polyol-tellurate complex is that
formed by the neutral ligand d-mannitol. Studies of this
complex by Edwards (9,10,11,12,14,15) and Lanese (25) indi-
cate that a one-to-one complex is formed. These investi-
gators have not considered that higher order complexes may
be possible. Since each mannitol molecule contains six
hydroxyl groups it is conceivable that three tellurate oxy-
anions could react with each ligand. A pH and conducto-
metric study by Gate and Richardson (26) revealed the exist-
ence of a 2Man.:3Te complex after a 10 day equilibration
period. Presumably this species would exhibit the following
structure:

```
                    OH
                    |
        H₂C—O       Te       O—CH₂
            \      /  \      /
        HC—O        O—OH      O—CH
                    |
        HC—O       Te       O—CH
            \      /  \      /
        HC—O        O—OH      O—CH
                    |
        HC—O       Te       O—CH
            \      /  \      /
        H₂C—O       O-       O—CH₂
```

The present investigation was undertaken with the
intention of contributing additional evidence to the
elucidation of polyol-tellurate complexes. A wide variety
of methods are available for studying complex ions and the
recent monograph by Rossotti and Rossotti (27) provides an
extensive summary. Being inclined toward electrochemistry,
a polarographic study was initiated. The use of polaro-
graphy in complex ion studies has been reviewed by Crow and
Westwood (28).

POLAROGRAPHY

Telluride, tellurite, and tellurate are known to be
polarographically active. The polarography of tellurium (VI)
has been established for some years. Nevertheless, there is
a certain lack of theoretical study, and where such studies

have been reported (29,30,31) there remains much room for further work and a necessity for correlating the results of earlier investigators.

Tellurium (VI) exhibits a well-defined, though irreversible, polarographic wave. In a coulometric investigation Norton et al (29) were able to show that the wave represents an eight electron reduction to the -2 oxidation state. It was noted that media containing complexing agents such as tartrate, citrate, and ammonia improved the definition of the cathodic waves. They did not establish whether this was a result of the formation of complexes with tellurium (VI) or a reduction product. Lanese (30) studied the anodic tellurium (VI) wave and discovered that tartrate distorts or eliminates it depending on the concentration.

POLAROGRAPHIC INVESTIGATION OF TELLURIUM (VI)

AND

POLYOL-ORTHOTELLURATES

APPARATUS AND MATERIALS

All polarographic measurements were made with a Sargent Model XXI recording polarograph. A Leeds and Northrup Type K-3 potentiometer (with an L&N 2435-C reflecting galvanometer and Weston Standard Cell) was used to obtain accurate e.m.f. values. For pH measurements a Leeds and Northrup Model 7405 expanded scale pH meter was employed. All chemicals were reagent grade with the exception of metatelluric acid which was obtained CP from the Amend Drug and Chemical Company, Inc.

A standard, non-thermostated, H-cell was used with a potassium chloride agar bridge and Saturated Calomel Electrode. A Fisher capillary under a 40 cm. mercury head was used for all experiments. Solutions were deaerated with water-saturated nitrogen for 15 minutes before each experiment. The S.C.E. was periodically checked with a Zinc (II) standard in 1M potassium nitrate. The half-wave potential is reported to be -1.012 volts vs. S.C.E. (29,32). The S.C.E. "went bad" several times during the course of this work and had to be renewed. A significant improvement in stability was noted when an H-cell with a larger diameter reference compartment was obtained.

Before any meaningful investigation of the complex

could be undertaken it was necessary for this investigator
to become familiar with the polarography of tellurium (VI).
The disadvantages of limited time and education made this
preliminary work more lengthy than originally expected.
An irreversible wave of this sort affords numerous inter-
esting, but time consuming, problems.

MEDIA

It was first thought that the Britton-Robinson uni-
versal buffer might be used to advantage at varying pH's.
The buffer is composed of a mixture of phosphoric, acetic,
and boric acids neutralized with sodium hydroxide. It was
prepared according to the directions of Müller (33). Un-
fortunately, in this medium, the limiting current of the
tellurium (VI) wave was not sufficiently separated from the
termination of the residual current, where hydrogen ions
are reduced.

This problem was extant at pH's as high as 10. At
low pH's no cathodic wave could be distinguished. This
rather unwieldy buffer was discarded in favor of a car-
bonate-bicarbonate system.

Previous investigators have demonstrated the useful-
ness of such buffers for studying the polarography of

tellurium (VI) and polyol-tellurate complexes (25,29). A

pH of 9.65 was chosen for the initial work. The cathodic

wave is suitably defined at this pH. In addition, Lanese

showed by a polarimetric investigation that the d-tartrate-

orthotellurate complex exists most conclusively at pH's

above 8 (21).

The ionic strength of the carbonate-bicarbonate buffer

was "beefed up" with potassium nitrate. A supporting

electrolyte of relatively high ionic strength, relative to

tellurate, permits the assumption of concentration inde-

pendent activity coefficients and a negligible cell

resistance.

CONCENTRATION STUDY

The relationship of the diffusion current to concen-

tration was found to be linear over a range of concentra-

tions from 1×10^{-5} to 1×10^{-2} Molar metatelluric acid.

The i_d/C ratio under the aforementioned conditions was 32.1

milliamps-liter-mole^{-1} (Fig. I). The diffusion currents

were measured at 1.5 volts vs. S.C.E., with a drop time $\underline{t}$

of 2.7 seconds, and a mercury flow rate $\underline{m}$ of 4.7 mg./sec.

The diffusion current constant, $I = i_d/Cm^{2/3}t^{1/6}$, is
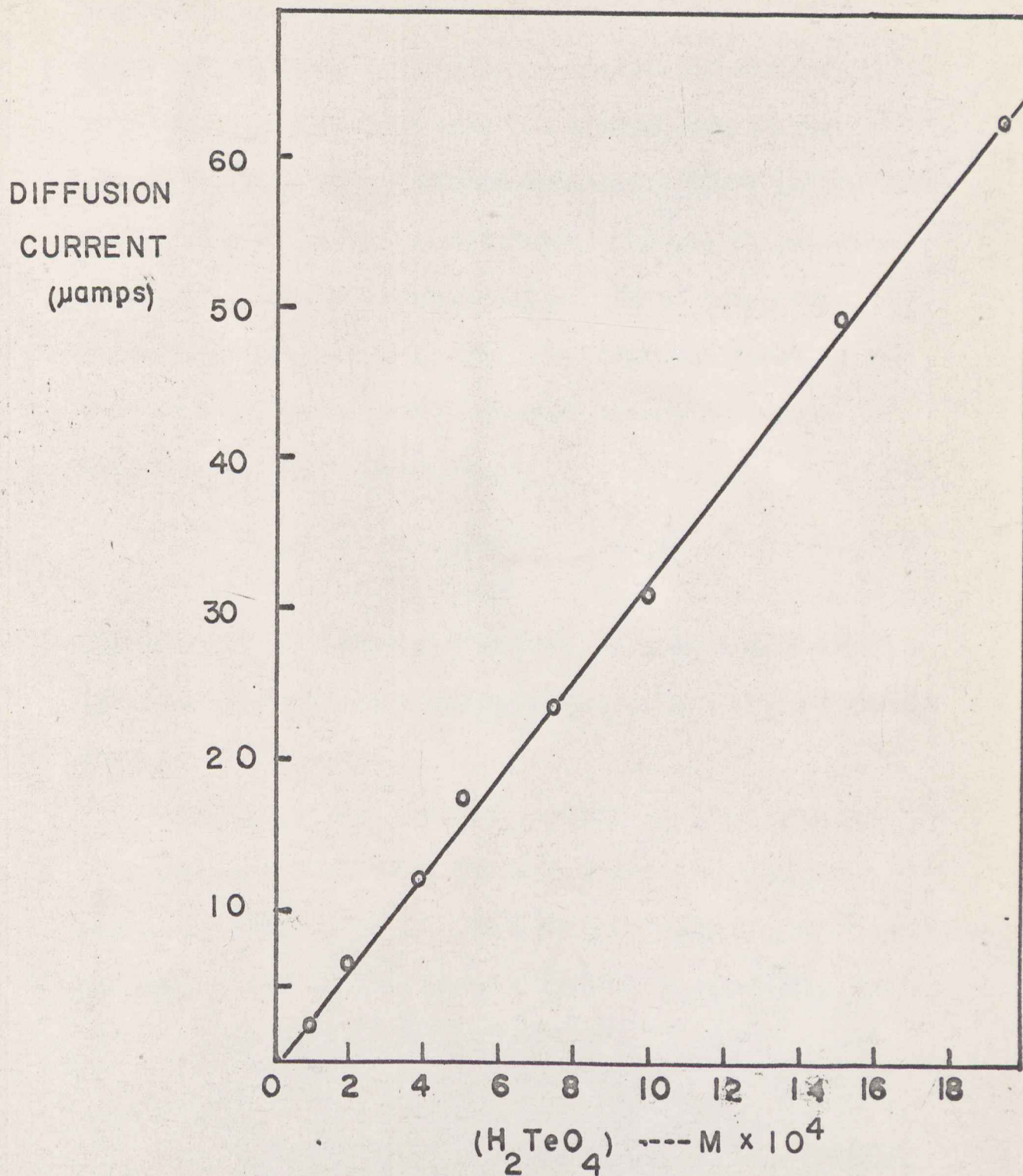
calculated to be 9.9 (34).

Fig. I.

The dependence of the diffusion current on the

molar concentration of tellurate in a carbonate-

bicarbonate buffer, pH 9.7

At tellurate concentrations above approximately 5×10^{-4} a very substantial maximum developed. Triton X-100 was found to be a suitable maximum suppressor.

At concentrations near .01 M streaming became visibly evident in the electrolyte and a black precipitate formed around the drop. Eventually the entire solution contained a suspended black solid. It is suspected, though not demonstrated, that the black substance is the free element (31). Telluride will reduce tellurate according to equation (III).

$$3Te^{-2} + Te^{+6} \longrightarrow 4Te^{o}. \qquad (III)$$
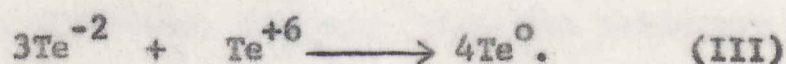
The apparent diffusion control of the wave height would indicate that this process occurs outside of the diffusion layer.

The anodic wave reaches a saturation current indicative of an electrode reaction limited by surface phenomena (30). A black precipitate formed by this reaction has been shown to be mercurous orthotellurate, $Hg_2H_4TeO_6$.

VARIATION OF THE MERCURY HEAD

The rate of mercury flow through a dropping mercury electrode is proportional to the pressure head above the

capillary tip. A slight variation is caused by an inter-
facial back pressure which has been neglected in the present
work. The Ilkovic equation for a diffusion-controlled
polarographic wave (IV), with all other things being equal,
reduces to (V), where $\underline{k}$ is a constant and $\underline{h}$ is the mercury
head in cm.

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6} \qquad\qquad \text{(IV)}$$

$$i_d = kh^{1/2} \qquad\qquad \text{(V)}$$

The observance of this proportionality is often used as a
criterion for diffusion control. That the tellurate wave
behaves in this manner is shown in Fig. II by the linear
plot of i_d vs. $h^{1/2}$. If the wave was controlled by a
chemical reaction in the diffusion layer (i.e., a kinetic
wave) the wave height would be independent of $\underline{h}$. For an
adsorption controlled wave the wave height is proportional
to $\underline{h}$.

ELECTROCAPILLARY DATA

Electrocapillary data were obtained for 1×10^{-4} $\underline{M}$
metatelluric acid in a carbonate-bicarbonate buffer of
pH 9.7 (Fig. III), and for the supporting electrolyte alone.
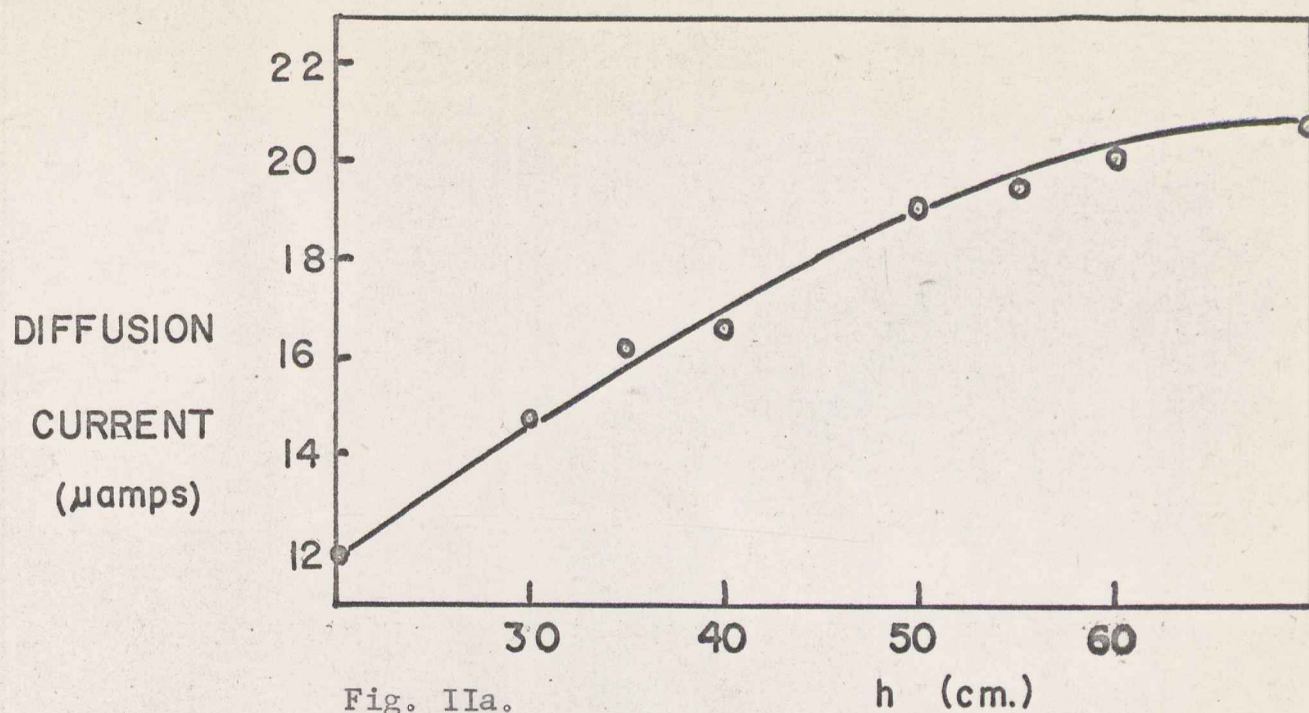The time for 25 drops was measured versus the potential every

DIFFUSION

CURRENT

(μamps)

22

20

18

16

14

12

30   40   50   60

h   (cm.)

Fig. IIa.

22

20

18

16

14

12

5   6   7   8

$h^{1/2}$
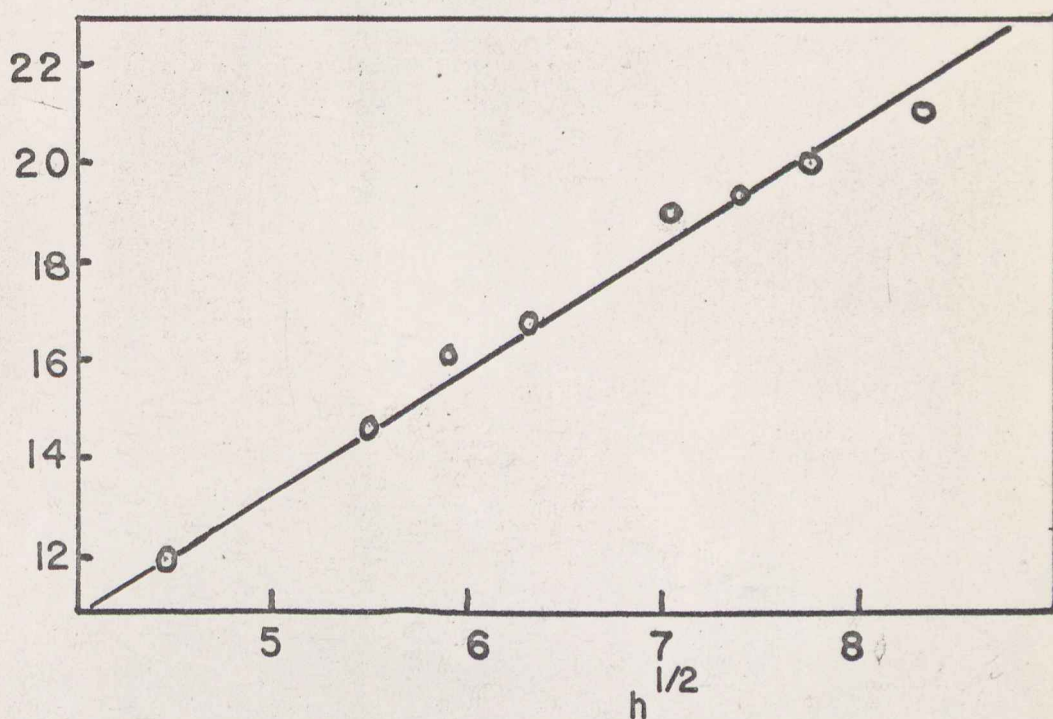
Fig. IIb.

The dependence of the diffusion current on the mercury head and the square root of the mercury head. $5 \times 10^{-4} \underline{M}$ tellurate in carbonate buffer, pH 9.6
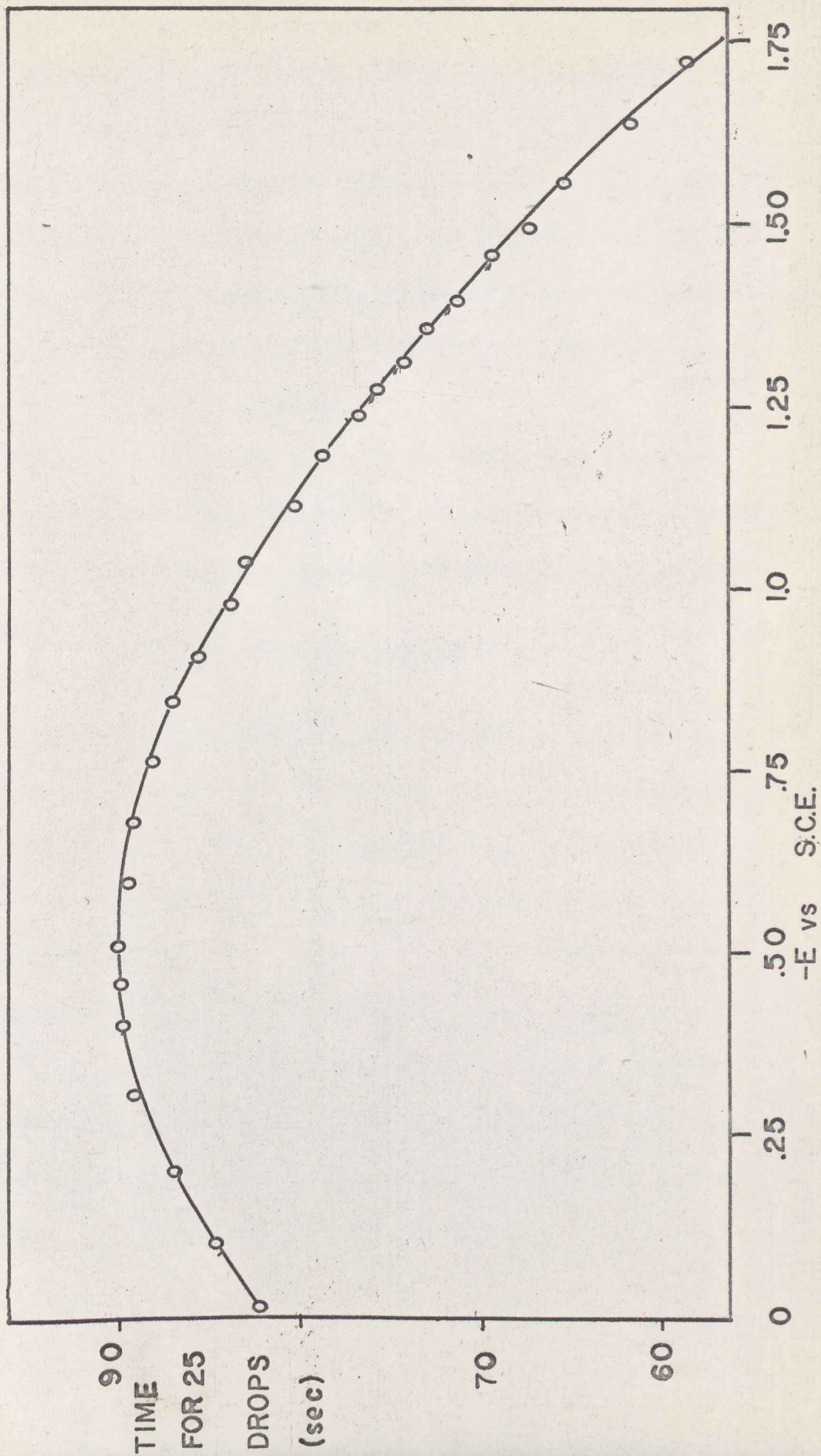
Fig. III. Electrocapillary Curve— 1 x 10^{-4} M tellurate in pH 9.7 carbonate buffer.

.05 volts from 0 to 1.8 volts vs. S.C.E. The two hyperbolic curves were found to be almost identical, both reaching a maximum at .52 volts vs. S.C.E.

This apparently regular behavior is in contrast to that of the anodic tellurium (VI) wave (30) and the cathodic tellurium (IV) wave (31). Both of these exhibit irregularities in their electrocapillary curves indicative of adsorption on the drop surface.

Although it is certain that the reduction involves eight electrons (29,31) the nature of the electrode process for the cathodic wave has eluded satisfactory explanation.

VARIATION OF IONIC STRENGTH

The effect of increasing the ionic strength was studied with 5×10^{-4} $\underline{M}$ metatelluric acid in a carbonate-bicarbonate buffer of pH 9.6_5 with an ionic strength of 0.21. Potassium nitrate was added in five steps bringing $\underline{I}$ from 0.21 to 1.81.

At the initial ionic strength of 0.21 the wave exhibited a very pronounced maximum followed by an erratic limiting current. The maximum completely disappeared when $\underline{I}$ was increased to 0.46. Over the series of six experiments the slope of the limiting current increased, becoming less

distinguishable from the hydrogen limit. This makes the accurate measurement of $E_{1/2}$ difficult at high ionic strengths. The half-wave potential moved positively from -1.36 to -1.30. The hydrogen background curve also moved positively.

This behavior indicates the necessity of careful ionic strength control when the cathodic wave is used to study a tellurate complex.

IRREVERSIBILITY PLOT

A reversible polarographic wave may be described by equation (VI).

$$E = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{i_d - i} \qquad (VI)$$

The slope of a plot of -E vs. log (i/i_d -i) will give a value of n consistent with the number of electrons involved in the polarographic reduction. Irreversibility plots for tellurate and polyol-tellurate complexes (Fig. IV) give values for n in the neighborhood of .05. This indicates that the cathodic tellurate wave is an extremely irreversible one since it is known to involve 8 electrons.
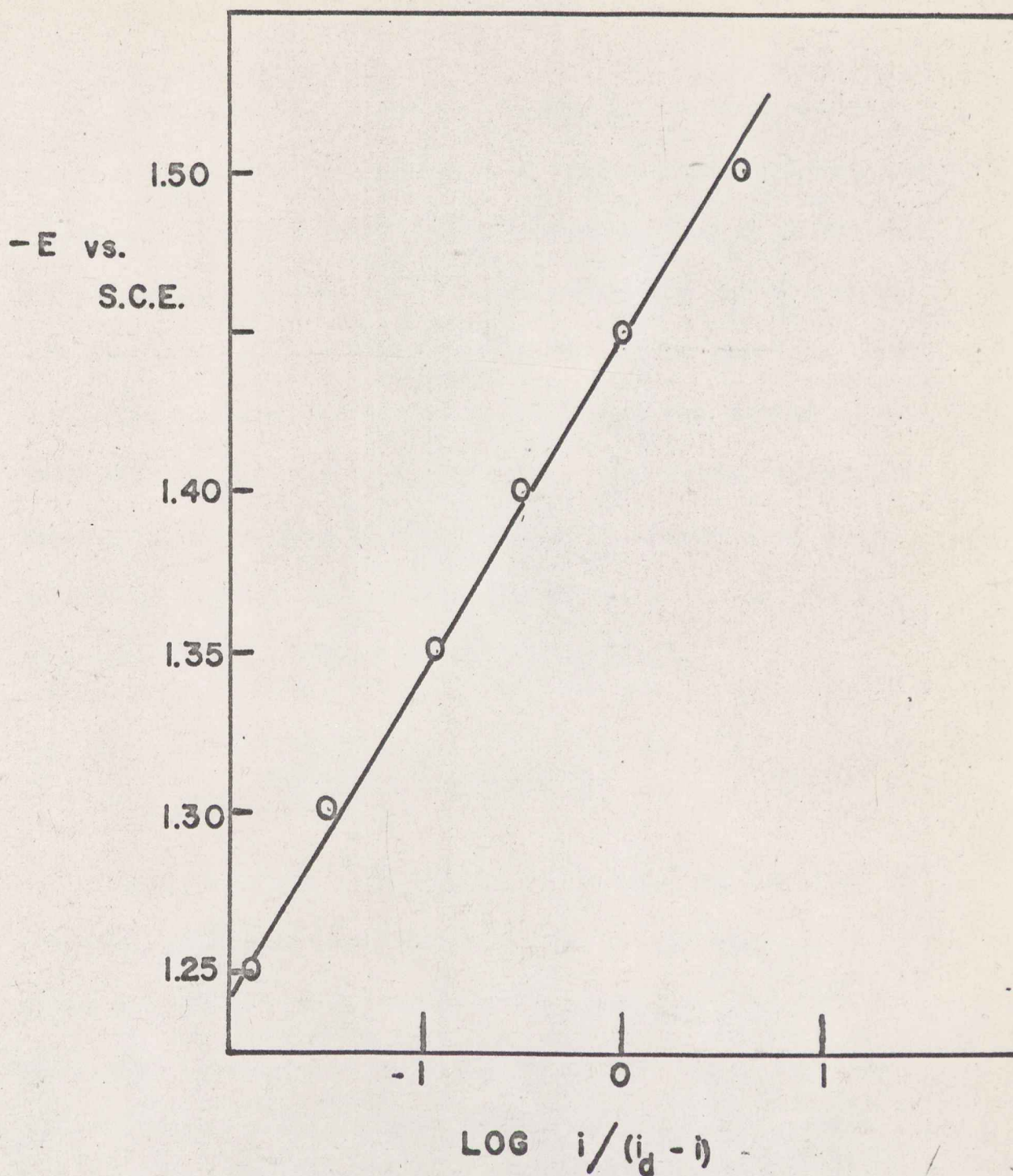
Fig. IV.
Irreversibility Plot for 2 X $10^{-4}\underline{M}$ tellurate and
5 X $10^{-3}\underline{M}$ mannitol in carbonate buffer, pH 10.5.

POLAROGRAPHY OF THE d-TARTRATE AND d-MANNITOL
TELLURATE COMPLEXES

The variation of the tellurate half-wave potential was investigated as a function of ligand concentration for the d-tartrate and d-mannitol complexes. For a reversible system it is possible to both determine the stoichiometry and stability of a polarographically active complex. The necessary relationships are derived from the Nernst equation and the Ilkovic equation (35). The stoichiometry is determined according to equation (VII), where p is the number of ligands per central group and C is the molar concentration of ligand in the electrolyte.

$$\frac{E_{1/2}}{\log C} = -0.05915 \frac{p}{n} \qquad \text{(VII)}$$

Polarography is certainly not a good method for studying tellurate complexes because of the extreme irreversibility. Aside from the irreversibility of the wave, the acidity of the tartrate ligand defies the purposes of the carbonate-bicarbonate buffer. The buffer capacity is not capable of handling the high concentrations of tartrate used here, however, constancy of pH is essential. It was necessary to add .2N NaOH to push the pH back to the

original 9.6_5. The ionic strength was thus maintained at about 0.2.

A series of experiments were run for both complexes and the resulting data were sporadic, inconsistent, and in-consequential. It was noticed, however, that the data collected for the mannitol complex was time dependent whereas the d-tartrate gave time independent results. This is illustrative of the very slow equilibration of mannitol-tellurate found by Gate and Richardson (26).

There are a number of ways in which irreversible polarography can be adopted to complex ion studies (28). One empirical method that can be applied to similar situations is to substitute an $\underline{\alpha n}$ term for $\underline{n}$. The $\underline{\alpha n}$ term is the value of "n" determined from an irreversibility plot. In the present work $\underline{\alpha n}$ is of the order of .05 and the empirical procedure does not improve the applicability of the $\Delta E_{1/2}$ data. Irreversibility being a matter of degree; it is suggested that the $\underline{\alpha n}$ "fudge factor" is useful only for much less irreversible situations.

OTHER METHODS

AND

SUGGESTIONS FOR FUTURE WORK

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Since the polarographic investigation provided little evidence with regard to complexation, and since time was short, it was decided to pursue the matter of the time dependence of the mannitol species with already proven methods.

A spectrophotometric investigation using the logarithm ratio method (36) was very successfully used to study the mannitol complex formed immediately after mixing the ligand and metal (i.e., a one-to-one complex). An attempt was made to duplicate the work of Lanese (25) and then follow the complexation versus time. Experiments were performed using both the Perkin-Elmer 202 and the Beckman DU ultraviolet spectrophotometers. These instruments are apparently incapable of the sensitivity of the more sophisticated Cary Model XI used by Lanese. No workable data could be obtained. This is one of the most applicable of the possible methods and it should be considered in the future.

Gate and Richardson (26) used the continuous variation method to investigate the d-mannitol and erythritol complexes. Variation of pH and conductivity showed that the 3Te:2Man. complex is predominant after about 10 days equilibration. Their data for mannitol was duplicated (with less sensitive

equipment) and the results confirmed.

A pH meter of sufficient stability and sensitivity was not available to permit the initiation of a pH study according to the procedures of Edwards (10).

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