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An indicator electrode for metal ions

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NOTE TO USERS

AN INDICATOR ELECTRODE FOR METAL IONS

by

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I. INTRODUCTION

Scientists have for several decades been aware of the important role played by the hydrogen ion concentration in the equilibria of aqueous solutions. As a result, several reliable potentiometric methods have been developed for its determination which do not disturb the equilibria of these solutions. The determination generally involves a single measurement of the potential of a cell which consists of a suitable reference electrode and an electrode reversible to hydrogen ions, called the indicator electrode. The most widely used indicator electrodes for hydrogen ions are the hydrogen electrode, the glass electrode and the quinhydrone electrode.

In comparison, the determination of metal ion concentration has not been developed to such a high degree; indeed, the polarographic method is the only generally applicable means of accomplishing this without disturbing the equilibrium of the solution. The potentiometric determination of metal ions, like the determination of hydrogen ions, involves measuring the potential between an electrode which is reversible to the metal ion in question, the indicator electrode, and a standard or reference electrode. The potential of the indicator electrode, called the single electrode potential, or half-cell potential, corresponding to a given half-cell reaction is related to the activities of the reacting substances by the Nernst equation

$$(1.1)\quad E = E^{\circ} - RT/nF \ln Q,$$

where: Q is a ratio of the product of the activities of the products

of the half-cell reaction to the product of the activities of the reacting substances each raised to the power of its coefficient in the half-cell reaction; E°, called the standard electrode potential, is the potential of the half-cell when all of the activities in Q are unity; n is the number of Faradays, F, involved per mole of chemical change; R is the universal gas constant, 8.314 joules/°C./mole; and T is the absolute temperature.

Perhaps the simplest and most common indicator electrode for metal ions consists of a piece of the solid metal dipping into a solution of its ions. Thus, measurement of the potential of a cell of the type

$$M;\ M^{+n},\ //\ KCl(0.10\ M.);\ Hg_2Cl_2;\ Hg$$

enables one to calculate the activity of M^{+n} by the equation

$$(1.2)\quad E + E_{SCE} = E^{\circ}_{M,M^{+n}} + 0.059/n \log (M^{+n}),$$

where the values of R, F and 2.303 have been substituted, and the temperature has been taken as 25°.

While cells of this type have been used extensively to determine standard potentials and equilibrium constants (1, 2, 3), they have not seen wide application in analytical chemistry. There are several reasons for this: (a) the EMF of such cells usually depends upon the physical state of the solid metal electrode, with the result that the EMF measurements often are neither constant nor reproducible; (b) many solid metal electrodes are attacked in acid solution, or oxidized by oxygen in alkaline solution, and thus cannot be used in such solutions; (c) such systems frequently attain equilibrium very slowly.

It is the purpose of this work to describe an electrode analogous to the quinhydrone electrode which is reversible to metal ions. The theory underlying its operation is developed and tested, and the experimental details of its use have been worked out.

II. HISTORICAL REVIEW

A. The Quinhydrone Electrode

The first reported application of a quinhydrone in analytical chemistry was the classic paper "Sur L'Hydrogenation des Quinhydrones" by Einar Biilmann in 1921 (4). In his paper Biilmann demonstrated that it was possible to determine the concentration of hydrogen ions in a solution by measuring the potential of the cell,

$$Pt;\ H^{+}(x\ M,\ satd.\ H_2Q_2)\ /\ KCl(3.5\ N);\ Hg_2Cl_2(s);\ Hg,$$

where ; indicates a phase boundary, and / a 3.5 N KCl agar bridge.

In developing the theory of the quinhydrone electrode, quinhydrone, which dissociates into one mole of hydroquinone and one mole of quinone in aqueous solution, is considered to have associated with it a certain pressure of hydrogen gas equal to that of an equivalent hydrogen electrode.

The constancy and reproducibility of potential measurements with the quinhydrone electrode were studied in dilute solutions of the strong acids, various organic acids and their salts and phosphate mixtures. Excellent results were reported in each case. Potentials of three quinhydrones, benzoquinhydrone, toluquinhydrone and xyloquinhydrone, were measured.

Sörensen (5) studied the effect of salts on the potential of the quinhydrone electrode and attributed the change in potential to a salt

effect on the solubility of the quinone and/or hydroquinone. To eliminate this difficulty he suggested that the solution be saturated with respect to quinone or hydroquinone and quinhydrone. These were termed, respectively, the "quinoquinhydrone" and "hydroquinhydrone" electrodes.

The standard reduction potentials of a number of other quinhydrone systems were also measured (6), among them the 2,4-dichloro- and 2,4-dibromobenzoquinhydrones, 1,2-dicyanoquinhydrone (7) and the corresponding chloro- and bromo-substituted toluquinhydrones.

The quinhydrone electrode, after its discovery by Biilmann, found almost immediate application in the determination of hydrogen ions. La Mer and Parsons (8) applied the electrode to acid-base titrations in biological systems. Harris (9) suggested and studied the use of the quinhydrone electrode for the estimation of amino acids and acid and basic functions. Kolthoff (10) studied the effect of protein on the potential of the quinhydrone electrode and its reliability as a hydrogen ion electrode in unbuffered and buffered solutions. He reports excellent reproducibility for the electrode up to pH 9 if the solution was well buffered, slightly lower if not well buffered. The new electrode was also used and recommended as a reference electrode (11), the reference solution being a solution of HCl (0.01 M) and KCl (0.09 M) saturated with benzoquinhydrone.

The following year Trene (12) described a simplified cell for the determination of pH with the quinhydrone electrode. In essence, it was a concentration cell of the type

$Pt;H_2Q_2$(satd), 0.01 N HCl, 0.09 N KCl // H^+(x M), H_2Q_2(satd.); Pt,

where the liquid junction is made by means of a diaphragm saturated with KCl. Other adaptions soon followed: Mislowitzer reported a new "double electrode" (13) in both macro- and micro- sizes; Mozolowski and Parnas (14) designed an electrode vessel about the size of the current glass electrode and which could be used repeatedly without replenishing the solid quinhydrone. This model approaches, if not exceeds, from the point of view of convenience, even the present-day glass electrodes.

As the understanding and development of the glass electrode progressed with the work of MacInnes and Dole (15) and others, the investigation and application of the quinhydrone electrode slowly waned, until in 1944 it practically disappeared from the laboratories.

B. The Chelate Rings

It is an inherent property of metal atoms, and in particular of those of the transition series of the periodic chart of the elements, that they form coordination compounds. Coordination, as used here, refers to the fact that both of the electrons having a part in the bonding were furnished by the "coordinating group"; it is, therefore, a distinction of the history of the bond rather than one based upon the nature of the bond itself.

When the coordinating group has two or more atoms which readily furnish a pair of electrons for coordination, a "chelate ring" is formed; the coordinating group is called a chelating agent, and the resulting compound a metal chelate compound (16). The term "chelate," according to Diehl (17), is derived from "chela," a Greek word referring to the claw of a lobster, and, therefore, appropriately connotes the ring structure and great stability of these compounds.

Two classes of donor atoms (donor groups) are usually recognised--acidic groups and coordinating groups. The formation of a bond between an acidic group and the metal is accompanied by the loss of a proton or hydrogen ion,[a] while in the case of the coordinating group the bond is formed by simple coordination.

Obviously, a chelating agent, if it has two donor groups, may have (a) two coordinating groups; (b) one acidic group and one coordinating group; and (c) two acidic groups. Two coordinating groups usually give rise to soluble complex ions such as ferrous tris-1,10-phenanthroline; one acidic and one coordinating group usually give rise to insoluble chelate compounds, since the charges of the metal ion are neutralised by the chelating agent; two acidic groups may give rise to either soluble complexes or insoluble salts.

The combination of an acidic and a coordinating group in a chelating agent is well illustrated by 8-hydroxyquinoline, which forms

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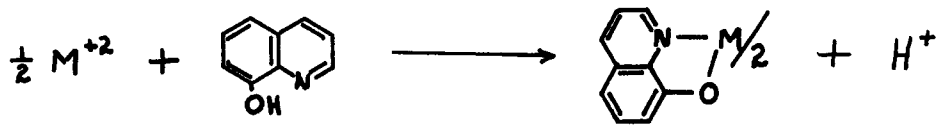
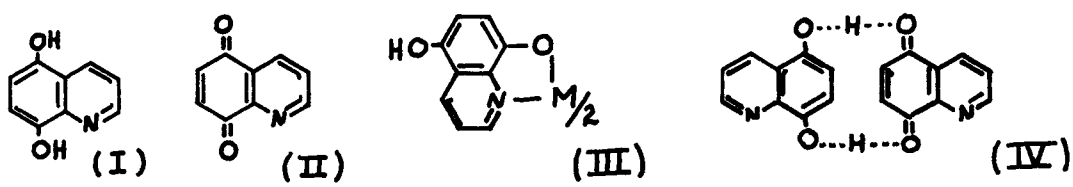
[a]This has been called a semi-polar double bond since an ionic character is added to the bond by the loss of the proton.

colored insoluble compounds with many of the transition metals.



Because of their insolubility, and in spite of their generally poor selectivity, these metal 8-hydroxyquinolates have found extensive use in analytical chemistry (18).

While there are no reports in the literature dealing with a quinhydrone oxidation-reduction system in equilibrium with metal ions, it was thought that this condition might be realized if the functions of both a reversible oxidation-reduction couple and of chelate ring formation could be combined in the same molecule. One such compound is 5,8-quinolinediol (I), which can be oxidized quantitatively and reversibly to 5,8-quinolinedione (II) or may combine with metal ions such as nickel, zinc or copper to form insoluble chelate derivatives (III). In addition, 5,8-quinolinediol (I) and 5,8-quinolinedione (II) combine to form 5,8-quinolinehydrone (IV) in a manner similar to benzoquinhydrone.



The preparation and oxidation of 5,8-quinolinediol to 5,8-quinolinedione were first reported by Fischer and Renouf (19) and later by a separate procedure by Matsmura and Sone (20). The quantitative oxidation of 5,8-quinolinediol by potentiometric titration has been reported.

In an earlier study 5,8-quinolinediol was found to form insoluble chelate compounds with nickel, copper(II), zinc, magnesium, cobalt(II) and iron(II). The composition of the precipitate obtained with nickel was shown to depend upon the pH at which the precipitation is carried out: at pH 5 and below, the precipitate contains four moles of 5,8-quinolinediol per mole of nickel; at pH 6 and above, it has the normal composition, two moles of 5,8-quinolinediol per mole of nickel, corresponding to the formation of chelate rings.

5,8-Quinolinehydrone has not been previously reported in the literature.

III. THEORY OF THE QUINHYDRONE ELECTRODE FOR METALS

The oxidation-reduction equilibrium between 5,8-quinolinedione and 5,8-quinolinediol is represented by the equation

$$Q + 2\,H^+ + 2\,e^- \rightleftharpoons H_2Q,$$

in which Q represents 5,8-quinolinedione and H_2Q represents 5,8-quinolinediol. The potential of this half cell is given in equation (1.1) as

$$(3.1)\quad E = E^\circ_{Q,H_2Q} + RT/2F \ln \frac{(Q)(H^+)^2}{(H_2Q)} \quad .$$

As previously mentioned, 5,8-quinolinediol under suitable conditions forms an insoluble salt with a number of bivalent metal ions, so that the following equilibrium also exists:

$$2\,H_2Q + M^{++} \rightleftharpoons M(HQ)_2 + 2\,H^+.$$

The equilibrium constant for the reaction as written is

$$(3.2)\quad K = \frac{M(HQ)_2\ (H^+)^2}{(H_2Q)^2(M^{++})} \quad .$$

Rearranging,

$$(3.3)\quad (H_2Q) = \frac{(M(HQ)_2)\ (H^+)^2}{K_1(H_2Q)(M^{++})} \quad ,$$

and substituting into equation (3.1), there results

$$(3.4)\quad E = E^\circ_{Q,H_2Q} + RT/2F \ln \frac{(Q)(H_2Q)(M^{++})}{K_1(M(HQ)_2)} \quad .$$

Since $M(HQ)_2$ is insoluble, its activity is unity by definition, so that

$$(3.5) \quad E = E^{o}_{Q,H_2Q} + RT/2F \ln \frac{(Q)(H_2Q)}{K_1} + RT/2F \ln (M^{++}) \quad .$$

If, further, 5,8-quinolinediol and 5,8-quinolinedione form a quinhydrone which is reasonably insoluble, the following equilibrium between 5,8-quinolinediol and 5,8-quinolinedione is also set up:

$$\underline{H_2Q_2} \rightleftharpoons H_2Q + Q \quad .$$

The equilibrium constant for this reaction, the solubility product of the 5,8-quinolinehydrone, is expressed as

$$(3.6) \quad K_2 = (H_2Q)(Q) \quad .$$

Substituting equation (3.6) into equation (3.5), converting to common logarithms and substituting values for T at 25°, R and F, equation (3.7) is obtained as follows:

$$(3.7) \quad E = E_{Q,H_2Q} + 0.059/2 \log (K_2/K_1) - 0.059/2 \, pM^{++} \quad ,$$

where pM^{++} is defined as the negative logarithm of the metal ion activity.

By measuring the potential of the cell,

$$Pt; M^{++}(x \text{ M. } \underset{\text{satd. } H_2Q_2}{\overset{\text{satd. } M(HQ)_2}{}}) \; // \; KCl(\text{satd.}); Hg_2Cl_2; Hg,$$

it is, therefore, theoretically possible to determine the activity of the metal ion by the equation

$$(3.8) \quad E = E^{o'} - 0.0591/2 \, pM.$$

The cell reaction may be represented by the equation

$$H_2Q_2 + M^{++} + 2\ Cl^- + 2\ Hg \rightleftharpoons M(HQ)_2 + Hg_2Cl_2 ,$$

where the reaction proceeds to the right when the electrode on the left of the cell is negative, and to the left when the calomel is negative.

Equation (3.7) is the fundamental equation for the electrode tested in this work. The graph of EMF *vs.* pM^{++} should be linear with a slope 0.059/2 and an intercept of $E^{o'} = E_{Q,H_2Q} + 0.059/2 \log (K_2/K_1)$.

Like benzoquinhydrone, 5,8-quinolinehydrone can function as a pH-indicating electrode. The theory, however, must be slightly modified, since 5,8-quinolinediol has an additional acidic group.

Consider the equilibria:

$$Q + 3\ H^+ + 2\ e^- \rightleftharpoons H_3Q^+$$

$$Q + 2\ H^+ + 2\ e^- \rightleftharpoons H_2Q$$

$$Q + H^+ + 2\ e^- \rightleftharpoons HQ^-$$

$$Q + 2\ e^- \rightleftharpoons Q^{--} ,$$

any one of which might under suitable conditions of pH be chosen to express the potential of the indicator electrode. It has been shown by the potentiometric neutralization titration of 5,8-quinolinediol hydrochloride, however, that up to pH 7 the reduced species is an equilibrium mixture of H_3Q^+ and H_2Q only. The oxidized or quinone species, however, shows only very weakly basic properties (19); it can be extracted from 10 per cent sulfuric acid with chloroform. It has

also been reported (19) that the hydrochloride of 5,8-quinolinedione can be obtained only after some standing in 25 per cent hydrochloric acid. Thus only the first two equilibria need be considered in deriving the relation between EMF and hydrogen ion activity.

The EMF of the first half-reaction above is, by equation (1.1),

$$(3.8)\quad E = E_1^o + RT/2F \ln \frac{(Q)(H^+)^3}{(H_3Q^+)} \quad ,$$

where H_3Q^+ is in equilibrium with H_2Q by the equation

$$H_3Q^+ \rightleftharpoons H_2Q + H^+ \ .$$

The equilibrium constant for this reaction, the acid dissociation constant, is

$$(3.9)\quad K = \frac{(H_2Q)(H^+)}{(H_3Q^+)} \quad .$$

Now let h and q be the total concentration of hydroquinone and quinone, respectively, in all states of acidic dissociation, and let m be the total quinhydrone, dissociating according to the equation

$$m \rightleftharpoons q + h,$$

so that if m is the only source of q and h,

$$(3.10)\quad q = h$$
$$(3.11)\quad Q = H_3Q^+ + H_2Q \quad .$$

Substituting the value of Q from equation (3.11) into equation (3.8:

$$(3.12)\quad E = E_1^o + RT/2F \ln \frac{[(H_3Q^+) + (H_2Q)]\ (H^+)^3}{(H_3Q^+)} \quad ,$$

and rearranging equation (3.13) is obtained:

$$(3.13)\quad E = E_1^o + RT/2F \ln\left\{(H^+)^3 \left[1 + (H_2Q)/(H_3Q^+)\right]\right\} .$$

Now by equation (3.9)

$$(H_2Q)/(H_3Q^+) = K_{a1}/(H^+) .$$

Substituting, introducing appropriate values for R, T and F, and rearranging, equation (3.14) is obtained:

$$(3.14)\quad E = E_1^o + 0.059/2 \log\left\{\left[1 + K_{a1}/(H^+)\right] (H^+)^3\right\}.$$

Eliminating (H^+) and separating terms, the following equation is finally arrived at:

$$(3.15)\quad E = E_1^o + .059/2 \log \left[(H^+) + K_{a1}\right] + .059/2 \log (H^+)^2 .$$

Equation (3.15) expresses the EMF of the half-cell as a function of (H^+). If this equation is differentiated with respect to log (H^+), the slope at any pH between zero and seven is

$$(3.16)\quad \frac{dE}{d(\log H^+)} = 0.059/2 \frac{(H^+)}{K_{a1} + (H^+)} + 0.0591 .$$

Now consider the limiting situations when E is plotted against pH:

(a) when $(H^+) = 1$, $E = E_1^o$,

(b) when $(H^+) >> K_{a1}$; $K_{a1} + (H^+) \simeq (H^+)$; slope = 0.089,

(c) when $(H^+) = K_{a1}$; $K_{a1} + (H^+) = 2(H^+)$; slope = 0.074,

(d) when $(H^+) << K_{a1}$; $K_{a1} + (H^+) \simeq K_{a1}$; $(H^+)/ K_{a1} + (H^+) =$ $1 - (K_{a1}/ K_{a1} + (H^+)] \simeq 0$; slope = 0.059 .

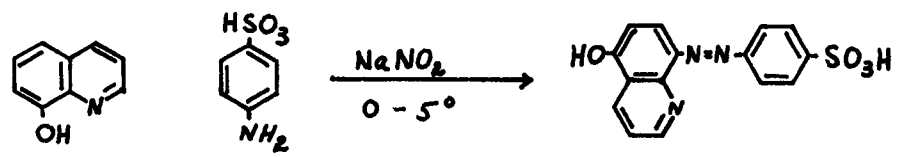
Thus the dependence of the potential of 5,8-quinolinehydrone is not linear with respect to pH throughout the range pH 1 to the pH 9 as is the case with benzoquinhydrone. A knowledge of the dependence of the potential of the system on pH will, however, prove to be valuable later in this work.

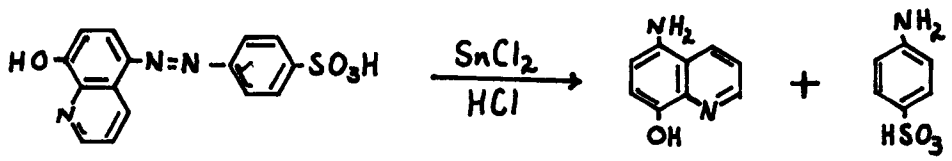
IV. EXPERIMENTAL WORK

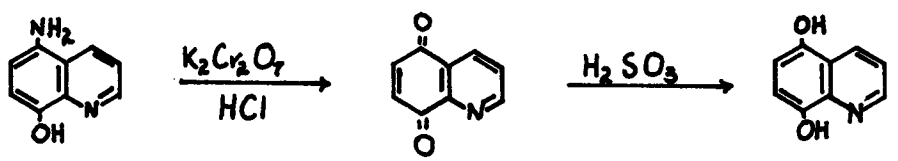
A. Preparation of Special Reagents

1. 5,8-Quinolinediol hydrochloride

5,8-Quinolinediol hydrochloride was prepared according to the procedure of Fischer and Renouf (19).







These authors carried out the oxidation of 5-amino-8-hydroxyquinoline to 5,8-quinolinedione in dilute sulfuric acid and obtained the sulfate salt of 5,8-quinolinediol upon subsequent reduction. In the present work a dilute hydrochloric acid solution (0.6 M) was found to be a more suitable medium for this step. 5,8-Quinolinediol hydrochloride was obtained as soft yellow-orange needles after several recrystallisations

from 10 per cent hydrochloric acid; m. p. with decomposition: 220° to 230°.

2. 5,8-Quinolinediol

The free base was prepared from 5,8-quinolinediol hydrochloride as follows. One g. of 5,8-quinolinediol hydrochloride was dissolved in 50 ml. of water and neutralized with an excess of sodium bicarbonate. The mixture was extracted immediately with three successive portions of ether, the combined extracts washed with a small amount of water and the ether solution then dried over anhydrous sodium sulfate. Evaporation of the ether yielded 0.60 g. of 5,8-quinolinediol; yield, 74 per cent. The pale yellow crystals melted at 181° to 183°; reported, 181° to 183° (19).

3. 5,8-Quinolinedione

5,8-Quinolinedione was prepared from 5,8-quinolinediol hydrochloride by the same procedure reported for the preparation from 5-amino-8-hydroxyquinoline by Petrow and Sturgeon (21). Two g. of 5,8-quinolinediol hydrochloride was dissolved in 10 ml. of 10 per cent sulfuric acid and oxidized with 1.00 g. of potassium bichromate in a little water. The mixture was immediately extracted four times with chloroform, washed with a little water and dried over anhydrous sodium sulfate. The combined extracts were concentrated to approximately 20 ml. and an equal volume of petroleum ether was added. Upon evaporation in air, 1.26 g. of yellow crystals of 5,8-quinolinedione was

obtained; yield 77 per cent. The crystals melted with decomposition at 111° to 112°; reported by Fischer and Renouf (19): 110° to 120°, with decomposition.

4. 5,8-Quinolinehydrone

5,8-Quinolinediol (0.546 g.) was dissolved in ether, and 0.539 g. of 5,8-quinolinedione was dissolved in an equal volume of petroleum ether. The warm solutions were mixed and the resulting solution was refluxed for one-half hour. Tiny black needles separated a short time after the solutions were mixed. The crystals were collected on a filter, recrystallized from ether-petroleum ether mixture and air-dried. The compound decomposed between 112° to 113°.

An amount of 32.40 mg. of the above crystals was dissolved in 50 ml. of 1.0 M perchloric acid and titrated with potassium bichromate, 0.0500 M. The titration was followed potentiometrically with a platinum-saturated calomel electrode system. The titration curve is shown in Figure 1. Calculation:

$$\frac{(4.22 \text{ ml.})(0.0500 \text{ meq./ml.})}{\frac{32.40 \text{ mg.}}{320.2 \text{ mg./mmol.}}} = 2.08 \text{ meq./mmol.} ,$$

where 320.2 is the molecular weight of $(C_9H_5O_2N)\cdot(C_9H_7O_2N)$.

The infra-red spectra of 5,8-quinolinediol (in nujol), 5,8-quinolinedione (in chloroform) and 5,8-quinolinehydrone (in nujol) were obtained with the Baird Associates Model B double-beam spectrophotometer. The spectra are shown in Figures 2, 3 and 4.

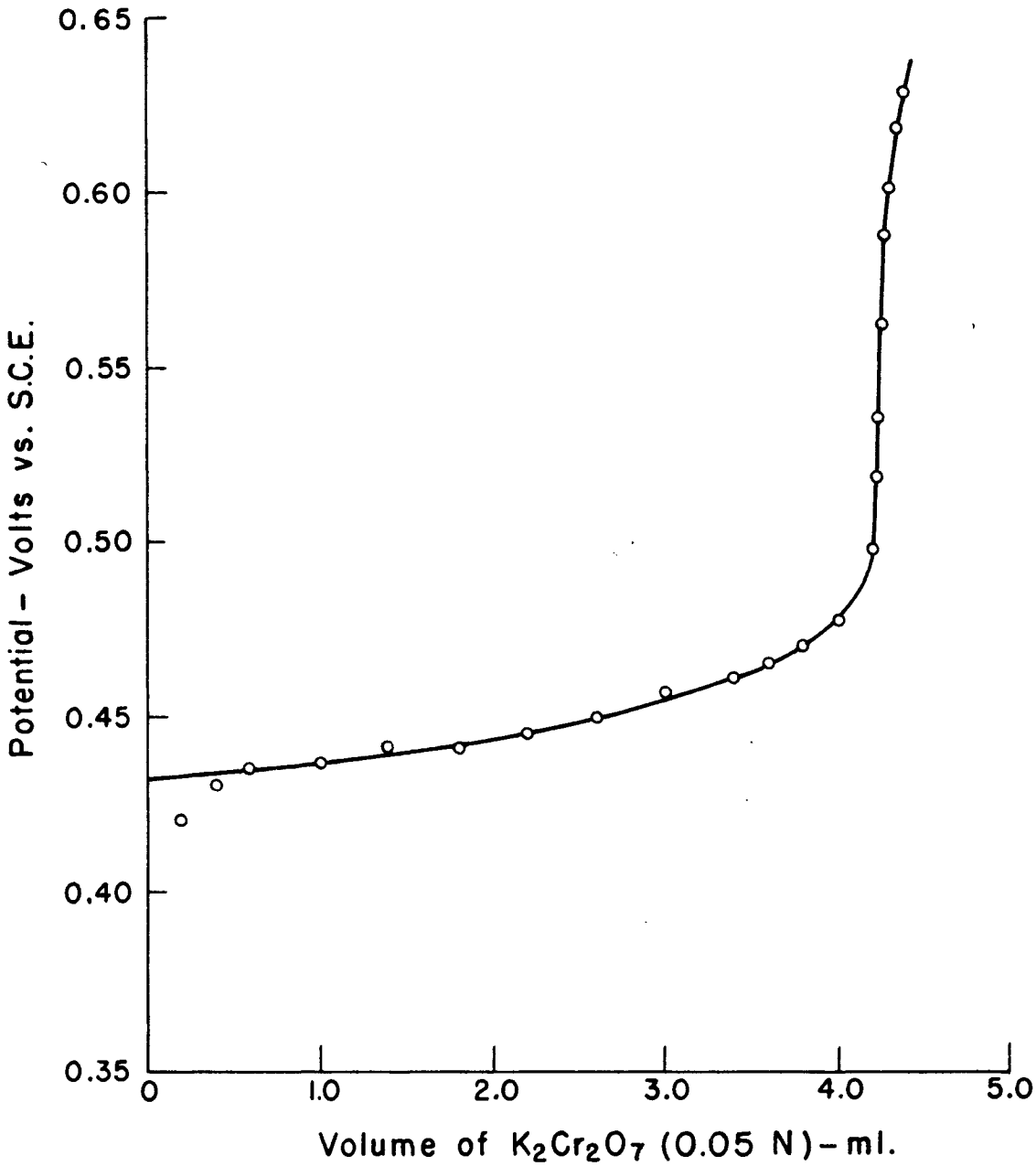
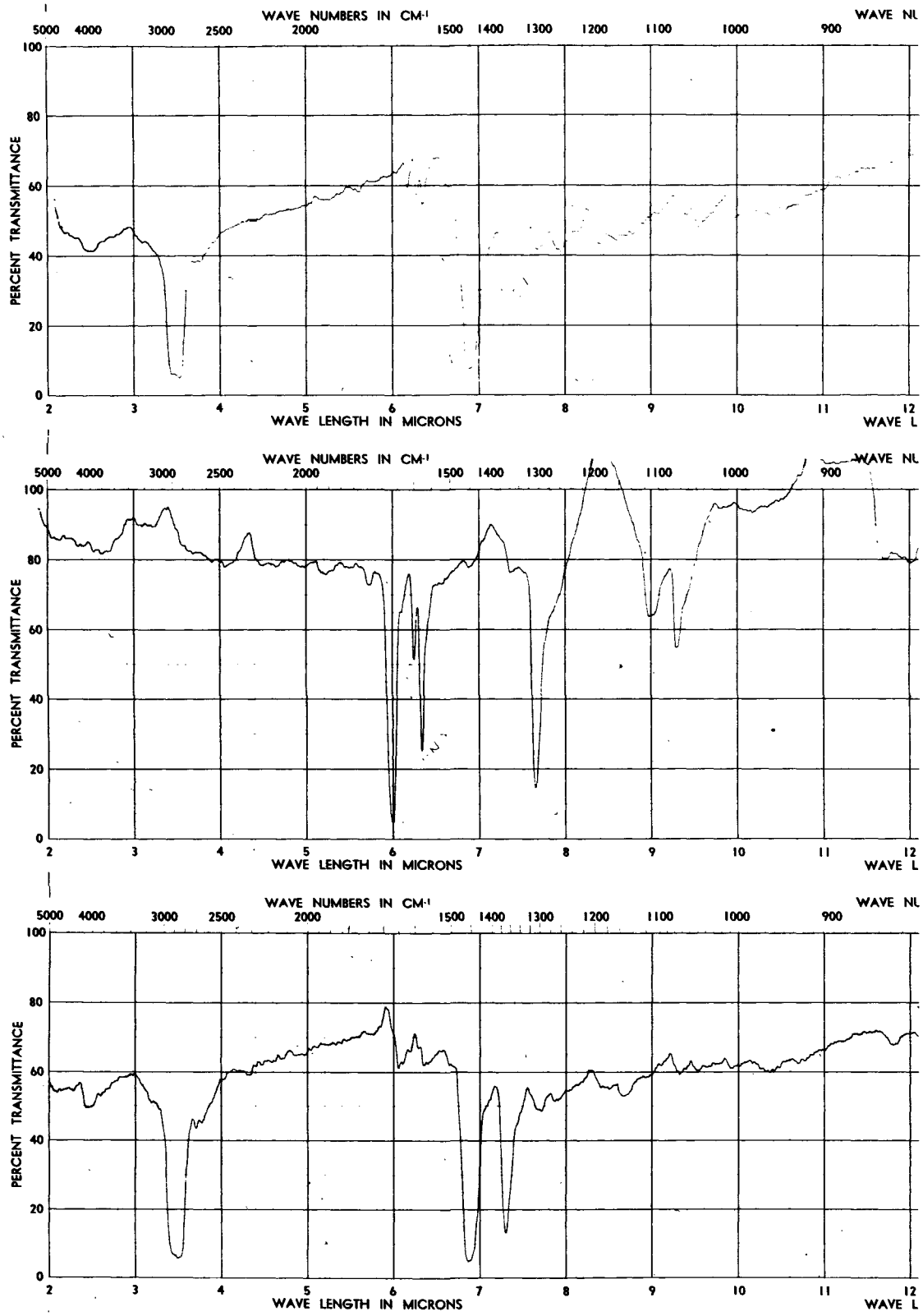


Figure 1. Potentiometric titration of 5,8-quinolinehydrone with potassium bichromate in 1.0 M perchloric acid

Figure 2. Infra-red spectrum of 5,8-quinolinediol in nujol

Figure 3. Infra-red spectrum of 5,8-quinolinedione in chloroform

Figure 4. Infra-red spectrum of 5,8-quinolinehydrone in nujol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5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900
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100 80 60 40 20 0
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WAVE L

5. Nickel(II) bis-5,8-quinolinediol

5,8-Quinolinediol hydrochloride, 400 mg. (2.0 mmol.) in 50 ml. of water, was added dropwise to a solution of 1.00 mmol. of nickel perchlorate in 50 ml. of water. The pH was maintained at pH 7 ± 0.5 by the dropwise addition of 0.10 N sodium hydroxide solution from a burette. A stream of nitrogen was passed through the solution to exclude oxygen. The system was stirred for one hour after the addition of reagents was complete.

The precipitate of nickel bis-5,8-quinolinediol was allowed to settle, the supernatant liquid was poured off and the precipitate was washed four times with water with intervening centrifugations. Finally the compound was dried in vacuum at 50° for three hours. The compound precipitated in this manner has been shown to have the composition $Ni(HQ)_2 \cdot x\ H_2O$ (22).

B. The Potential of 5,8-Quinolinehydrone As a Function of pH
The E^o of the System $Q + 2\ H^+ + 2\ e^- = H_2Q$

1. Reagents

A series of buffer solutions of ionic strength 0.10 was prepared covering the range pH 1 to 10. The composition of the buffers with their approximate pH is given in Table 1.

Crystalline reagent-grade buffer salts (meeting ACS specifications) were used in the preparation of this series of buffers. Reagent-grade

Table 1. Composition and Ionic Strength of Some Buffer Solutions

	Composition	Ionic strength	pH
1.	HCl (0.10 M)	0.10	1.09
2.	HCl (0.01 M) KCl (0.09 M)	0.01 0.09	2.10
3.	Citric acid (0.01 M) KCl (0.098 M)	0.0025 0.098	2.62
4.	Potassium acid tartrate (0.03 M) KCl (0.064 M)	0.036 0.064	3.57
5.	Potassium acid phthalate (.05 M) KCl (0.047 M)	0.053 0.047	4.01
6.	Acetic acid (0.10 M) Sodium acetate (0.10 M)	 0.10	4.66
7.	KH_2PO_4 (0.045 M) K_2HPO_4 (0.005 M) KCl (0.04 M)	0.045 0.015 0.040	5.90
8.	KH_2PO_4 (0.025) (N. B. S. Standard) Na_2HPO_4 (0.025)		6.860
9.	Sodium tetraborate (0.01 M) KCl (0.08 M)	0.02 0.08	9.18
10.	Sodium carbonate (0.025 M) Sodium bicarbonate (0.025 M)	 0.10	10.02

potassium chloride was used to adjust the ionic strength to 0.10, and the salts were dissolved and diluted to volume with deionized, distilled water. The ionic strengths listed for the buffer salt-acid systems alone are those reported by Bates et al. (23). The hydrochloric

acid and acetic acid buffers were standardised by titrating with 0.1088 N sodium hydroxide.

The hydrogen used was a highly pure product, prepared by the electrolytic process for liquefaction work in the low temperature laboratory of the Physics Department, Iowa State College.

2. Apparatus and procedure

The cell employed for the EMF measurements was a standard size, 8 cm. x 4 1/2 cm., glass weighing bottle. The cap was adapted to permit the introduction of the electrodes through snugly fitting sleeves and was fitted to the bottle itself with a ground-glass joint.

Solutions for measurement were brought to and maintained at 25 $\pm$ 0.02° C. in a precisely thermostated water bath. All potentials were measured with a Leeds and Northrup Type K potentiometer; the standard cell was calibrated with a cell recently checked by the National Bureau of Standards. The potential balance was indicated by a Leeds and Northrup lamp and scale galvanometer having a sensitivity of 0.50 microvolts per millimeter. The final assembly is pictured in Figure 5.

The pH of the buffer solutions was determined with a hydrogen electrode used in conjunction with a saturated calomel electrode. The platinised platinum electrode was prepared and assembled in the manner described by Perley (24). The pH values reported are based upon two

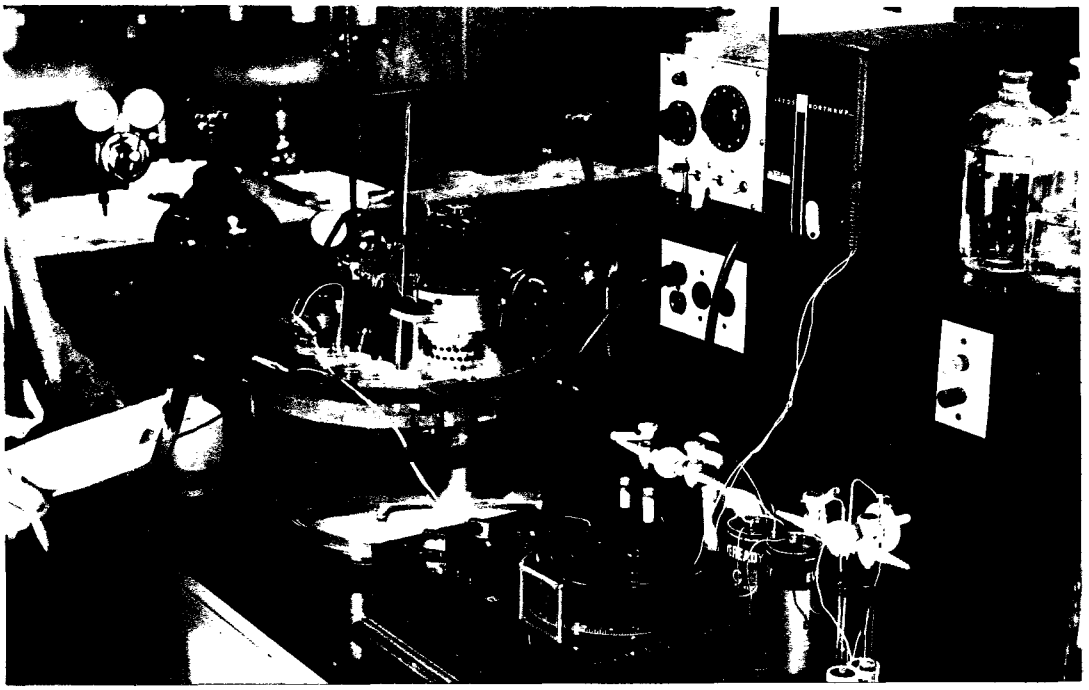


Figure 5. Assembly of the apparatus for potential measurements

successive EMF measurements which agreed within 0.1 millivolt and were calculated by the equation

$$pH = (E - E^{\circ})/0.0591,$$

where E° was determined by measuring the EMF of the same cell when it contained the N. B. S. mixed phosphate buffer, pH 6.860 at 25°.

The EMF of the quinoline dione-quinolinediol system was measured with the apparatus described above. The cells, carefully cleaned and rinsed with the solutions to be measured, were filled and placed in the constant temperature bath. Nitrogen, previously purified by passage through 0.1 M vanadium(II) sulfate solution, 10 per cent sodium hydroxide solution, water and a portion of the solution to be measured, was passed through the cell in a slow stream for a period of 30 to 45 minutes. A small amount, 1 to 2 mg., of 5,8-quinolinehydrone was carefully introduced through a small port in the cell top. Steady potentials were usually obtained within 30 minutes after the addition of the reagent; the results reported were constant to ± 0.2 millivolts for a period of five minutes. The data are summarized in Table 2 and are shown graphically in Figure 6.

3. Results

The slope of the curve of Figure 6 in the acid region is found experimentally to be 0.081 compared to the predicted value of 0.089. If this portion of the curve is extrapolated to pH 0, the value of the ordinate gives the standard potential for the half-reaction $Q + 3\,H^{+} + 2\,e^{-} \rightleftharpoons H_3Q^{+}$. The value so obtained is 0.416 volts *vs.* S.C.E.

Table 2. Hydrogen electrode and 5,8-quinolinehydrone electrode potentials of some buffer solutions at 25°

Buffer	EMF, H elec. (volts)	pH	EMF Pt - SCE (volts)
1	- 0.3061	1.09	0.3470
2	- 0.3649	2.09	0.2647
3	- 0.3960	2.61	0.2270
4	- 0.4501	3.53	0.1505
5	- 0.4757	3.96	0.1180
6	- 0.5176	4.67	0.0555
7	- 0.5886	5.88	- 0.0406
8	- 0.6471	6.860*	- 0.0962
9	- 0.7806	9.13	- 0.2058**
10	- 0.8312	9.97	- 0.260 **

*N. B. S. standard buffer.

**Potential drifted badly.

The standard potential, E°_2, for the half-reaction $Q + 2\,H^+ + 2\,e^- \rightleftharpoons H_2Q$ can be calculated from the measured value, E°_1, above very simply as follows. Consider again the equilibria just listed, either of which may be chosen to express the potential of a solution containing the above species. Hence,

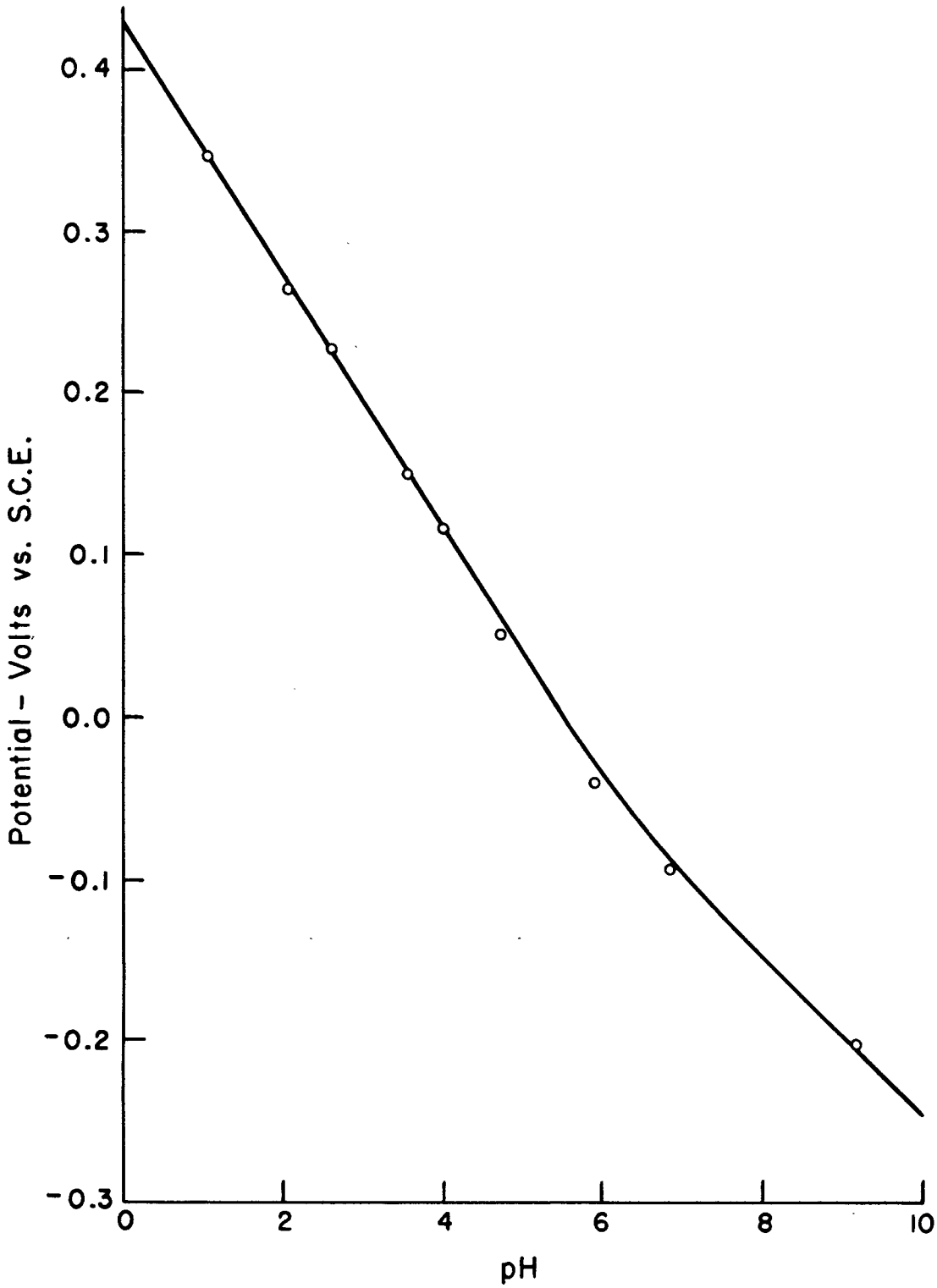


Figure 6. Potential of 5,8-quinolinehydrone as a function of pH

$$(4.1)\quad E = E^{\circ}_1 + .0591/2 \log \frac{(Q)(H^+)^3}{(H_3Q^+)} \ ,$$

and $$(4.2)\quad E = E^{\circ}_2 + .0591/2 \log \frac{(Q)(H^+)^2}{(H_2Q)} \ .$$

Equating equations (4.1) and (4.2),

$$(4.3)\quad E^{\circ}_1 + .0591/2 \log \frac{(Q)(H^+)^3}{(H_3Q^+)} = E^{\circ}_2 + \frac{.0591}{2} \log \frac{(Q)(H^+)^2}{(H_2Q)} \ .$$

Now, $$H_3Q^+ \rightleftharpoons H_2Q + H^+ \ ,$$

so that

$$(4.4)\quad K_{a1} = (H_2Q)(H^+)/(H_3Q^+) \ .$$

Combining equations (4.3) and (4.4) and eliminating (H_3Q^+), there results,

$$(4.5)\quad E^{\circ}_1 + .0591/2 \log K_{a1} = E^{\circ}_2$$

$$(4.6)\quad E^{\circ}_2 = E^{\circ}_1 - .0591/2\ pK_{a1} \ .$$

The value previously reported for pK_{a1} is 4.5, as determined from the midpoint of the neutralisation titration curve. Substituting this with the experimentally determined value of E°_1 into equation (4.6), one calculates $E^{\circ}_2 = 0.281$ volts *vs.* S. C. E.

4. Discussion

The standard potential, E°_1, of the half-cell reaction, $Q + 3\ H^+ + 2\ e^- \rightleftharpoons H_3Q^+$, has been measured, and from it the standard potential, E°_2, of the half-reaction, $Q + 2\ H^+ + 2\ e^- = H_2Q$, has been calculated. The experimental curve of pH *vs.* EMF of the

5,8-quinolinehydrone system does not show exact agreement with the curve predicted theoretically; however, the curve is sufficiently well defined in the acid region to permit the reasonably precise determination of E°_{1}. The value obtained, +0.662 volts (hydrogen scale), is in good agreement with the value +0.666 volts determined from the mid-point of the potentiometric oxidation titration curve of 5,8-quinolinediol hydrochloride in 1.0 M perchloric acid (22).

C. The Potential of the System 5,8-Quinolinedione-5,8-Quinolinediol As a Function of Nickel Ion Concentration

1. Reagents

a. Stock nickel perchlorate solution. Pure Mond nickel, 0.5860 g., was dissolved in two to three ml. of perchloric acid, and the solution evaporated to dryness on a steam plate under a heat lamp. The residue was dissolved in deionized, distilled water and diluted to one l. The resulting solution was 0.0100 M.

b. Stock sodium acetate-acetic acid buffer. Reagent-grade sodium acetate, 27.22 g., and 0.726 g. of reagent-grade glacial acetic acid were dissolved, mixed and diluted to two l. with deionized, distilled water.

c. Stock sodium fluoride-hydrofluoric acid buffer. Reagent-grade sodium fluoride, 8.4 g., was dissolved and diluted to two l. with deionized, distilled water. Just sufficient concentrated hydrofluoric acid (a few drops) was added to bring the pH to 5.93. The resulting solution was 0.10 M in sodium fluoride.

d. Stock sodium fluoride (1.00 M)-hydrofluoric acid buffer. Reagent-grade sodium fluoride, 42.0 g., was dissolved and the pH adjusted as in (c) above.

e. Stock sodium fluoride (5/9 M)-hydrofluoric acid buffer. Reagent-grade sodium fluoride, 23.33 g., was dissolved and diluted to one l. and the pH adjusted as in (c) above.

f. Stock sodium acetate (1.00 M)-acetic acid (0.05 M). This was prepared as in (b) above.

g. Trimethylacetic acid-sodium trimethylacetate solution. Eastman Kodak trimethylacetic acid, 10.21 g., was dissolved in 700 ml. of deionized, distilled water and neutralized to pH 6 with standard 0.1 N sodium hydroxide solution. The resulting solution was diluted to one l.

2. Apparatus and procedure

The apparatus employed is exactly that described in the preceding section. The solutions to be measured were placed in a rack in the constant temperature bath, and nitrogen was allowed to pass through the solutions for approximately 45 minutes to remove oxygen. A small amount, two to three mg., of nickel bis-5,8-quinolinediol and a like amount of 5,8-quinolinehydrone were introduced through a small port in the top of the cell. The potential of the platinum-S.C.E. system was measured and recorded when it became and remained constant to within

± 0.1 millivolts for a period of five to ten minutes. A slow stream of nitrogen passed through the solution during the measurement.

Except where otherwise specified, pH measurements were made with a Beckman Model G pH meter calibrated with the National Bureau of Standards mixed phosphate buffer at pH 6.860.

Solutions for measurement were prepared by pipetting the appropriate amount of standard nickel perchlorate solution and stock buffer solution, and diluting to 250 ml. Where this procedure was not feasible, the required amount of nickel perchlorate solution was evaporated to dryness and redissolved in a buffer of the desired concentration and pH.

3. Results

a. Unbuffered nickel solutions. Standard nickel perchlorate solutions covering the range pNi 1 to 7 were prepared and the potential was measured as just described. The potentials commonly showed rather serious drifting over a range of approximately five millivolts and, in general, were not reproducible. The results are summarized in Table 3 and are shown graphically in Figure 7.

b. Nickel perchlorate in sodium acetate(0.10 M)-acetic acid (0.006 M) solutions. Solutions for measurement were prepared as described in section b under Reagents. Potentials were measured as described above. Steady potential values were obtained, usually within 30 minutes, and the values recorded when they remained constant for a

Table 3. The potentials of 5,8-quinolinedione-5,8-quinolinediol in unbuffered nickel perchlorate solutions saturated with 5,8-quinolinehydrone and nickel bis-5,8-quinolinediol

Soln.	$Ni(ClO_4)_2$	pNi	EMF (S.C.E.) (volts)
1	0.010	2.00	0.0830
2	0.0030	2.52	0.0530 (drifting)
3	0.0010	3.00	0.0545
4	5.0×10^{-4}	3.30	0.0321 (drifting)
5	1.0×10^{-4}	4.00	0.0125
6	5.0×10^{-5}	4.30	- 0.0035
7	1.0×10^{-5}	5.00	- 0.0065 (drifting)

period of five to ten minutes. The average reproducibility over the entire range of pNi measured was $\pm$ .5 millivolts. The results are listed in Table 4 and are plotted graphically in Figure 7. Activity coefficients are from Curtman and Edmonds (25a), "Calculations of Qualitative Analysis," p. 57 (1941). Measurements of pH on a large number of solutions revealed no difference in pH before and after the EMF measurements were made.

c. Nickel perchlorate in sodium fluoride-hydrofluoric acid solutions. Three series of standard nickel perchlorate solutions in 0.10 M sodium fluoride, 0.50 M sodium fluoride and 1.0 M sodium fluoride,

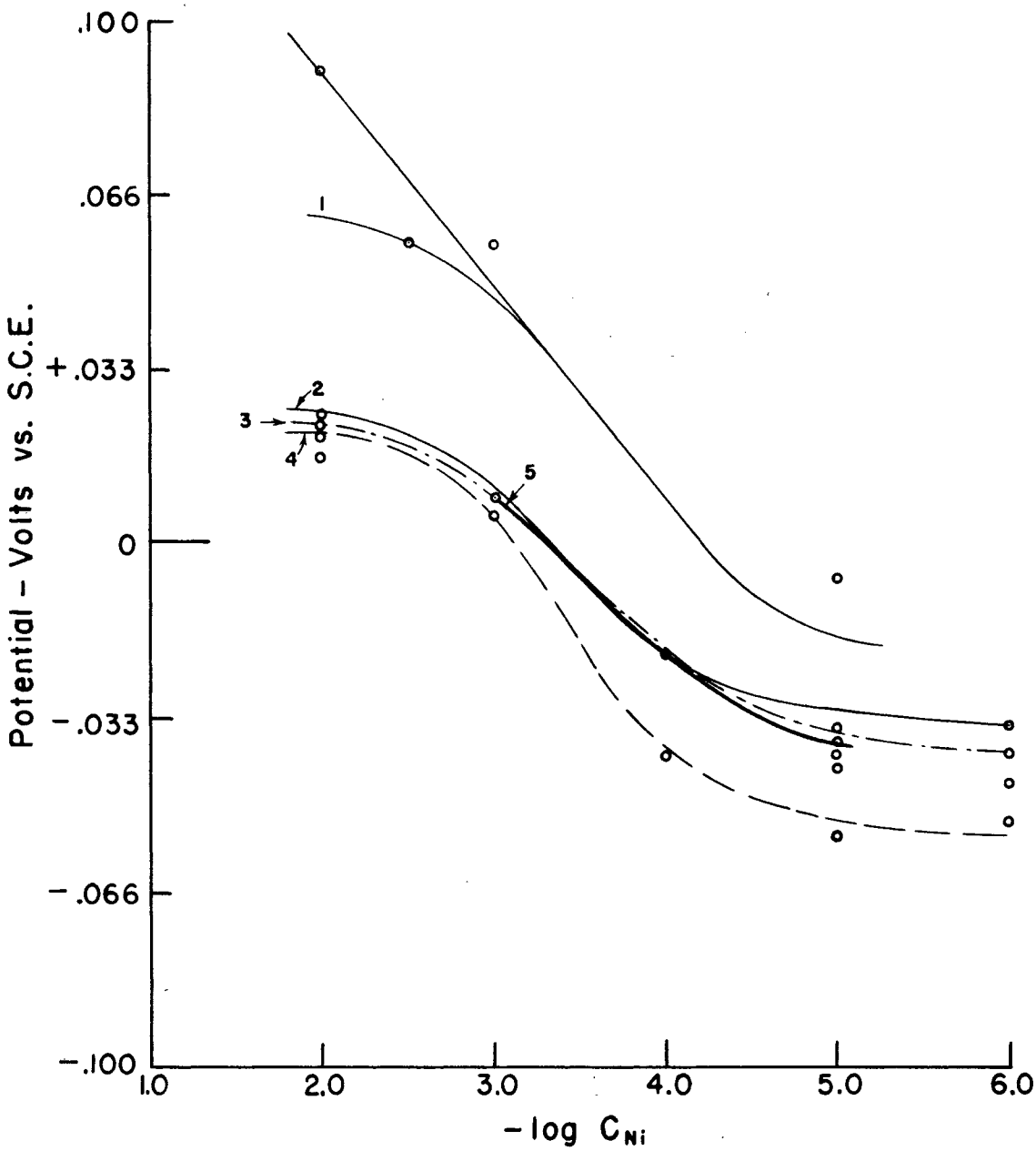


Figure 7. Potential of 5,8-quinolinehydrone as a function of nickel concentration in various buffer systems

Table 4. The potentials of 5,8-quinolinedione-5,8-quinolinediol in nickel perchlorate solutions buffered with sodium acetate-acetic acid and saturated with 5,8-quinolinehydrone and nickel bis-5,8-quinolinediol

$Ni(ClO_4)_2$	μ	$f_{\pm}(Ni^{++})$	pNi	pH	EMF (S.C.E.) (volts)
0.01	0.13	0.37	2.43	5.88	0.0245 0.0249
0.001	0.11	0.39	3.41	5.90	0.0089 0.0102
0.0001	0.10	0.40	4.40	5.90	- 0.0236 - 0.0236
0.00001	0.10	0.40	5.40	5.90	- 0.0327 - 0.0311
0.000001	0.10	0.40	6.40	5.91	- 0.0349 - 0.0360
Buffer only				5.90	- 0.0349

respectively, were prepared and adjusted to pH 6 by the addition of a few drops of concentrated hydrofluoric acid. Serious drifting of the potential was observed when measured in the usual manner. The pH of the solutions was measured before and after measurement of the 5,8-quinolinehydrone potential, and these values are reported with the EMF data in Table 5.

The sodium fluoride-hydrofluoric acid buffer system has almost no buffer capacity toward alkali at pH 6. Even the 1.0 M sodium fluoride buffer shows the variation of pH and unsteady potentials characteristic

Table 5. The potentials of 5,8-quinolinedione-5,8-quinolinediol in nickel perchlorate solutions buffered with sodium fluoride-hydrofluoric acid and saturated with 5,8-quinolinehydrone and with nickel bis-5,8-quinolinediol

$Ni(ClO_4)_2$	$-\log C_{Ni}$	pH (before)	pH (after)	EMF (S.C.E.) (volts)
0.01	2.00	6.0	6.4	0.02
0.001	3.00	6.0	6.5	- 0.006
1.0×10^{-4}	4.00	6.0	6.6	- 0.040
1.0×10^{-5}	5.00	6.0	6.6	- 0.057
1.0×10^{-6}	6.00	6.0		- 0.053

of the unbuffered system. The results are shown graphically in Figure 7.

4. Nickel perchlorate in trimethylacetic acid-sodium trimethylacetate solutions

Solutions for measurement were prepared in the same manner as the sodium acetate-acetic acid buffered solutions. The potentials measured are summarized in Table 6 and are plotted in Figure 7.

While reports of the formation of complex ions of nickel by coordination with oxygen are few (25b), it was considered possible that nickel ion was being complexed by acetate ion in the acetic acid-sodium acetate buffered systems. To test this proposition, and perhaps determine the ionic strength effect on the measured potential of these systems, a

Table 6. The potentials of 5,8-quinolinedione-5,8-quinolinediol in nickel perchlorate buffered with trimethylacetic acid-sodium trimethylacetate and saturated with 5,8-quinolinehydrone and with nickel bis-5,8-quinolinediol

Soln.	$Ni(ClO_4)_2$	-log C_{Ni}	pH	EMF (S.C.E.) (volts)
2	0.010	2.00	5.95	0.024 (unst)
	0.010	2.00	5.99	0.025 (unst)
3	0.001	3.00	5.98	0.0089
	0.001	3.00	5.98	0.0091
4	0.0001	4.00	5.98	- 0.0254
	0.0004	4.00	5.98	- 0.0228
5	1.0 x 10	5.00	5.98	- 0.0430
	1.0 x 10	5.00	5.98	- 0.0375
6	Buffer soln. alone		5.98	- 0.0469

series of solutions was prepared in which the concentration of sodium acetate and acetic acid were varied, while the ratio of $(NaC_2H_3O_2)/(HC_2H_3O_2)$, and hence the pH, was held constant. The $Ni(ClO_4)_2$ concentration was held constant at 0.001 M.

Solutions for measurement were prepared by taking 25.0 ml. of standard nickel perchlorate solution, 0.01 M, and varying known amounts of a stock sodium acetate-acetic acid buffer solution (NaAc, 1.00 M; HAc, 0.05 M), and diluting to 250 ml. The final concentration of nickel perchlorate thus was 0.001 M for each solution, and the final ratio $(NaC_2H_3O_2)/(HC_2H_3O_2)$ remained constant.

The EMF of the Pt-S.C.E. system in these solutions was measured as described above. The pH was measured before and after the EMF measurements, and no change in pH was observed in any case. These results are summarized in Table 7.

Table 7. The potentials of 5,8-quinolinedione-5,8-quinolinediol at varying ionic strengths in 10^{-3} M nickel perchlorate and saturated with 5,8-quinolinehydrone and nickel bis-5,8-quinolinediol

Soln.	pH	(NaAc)	μ	log (NaAc)	EMF (S.C.E.) (volts)
1	6.00	0.80	0.80	- 0.10	- 0.0070 - 0.0070
2	5.96	0.40	0.40	- 0.39	- 0.0004 - 0.0005
3	5.98	0.10	0.10	- 1.00	0.0052 0.0074 0.0063 0.0071
4	5.97	0.06	0.063	- 1.22	0.0087 0.0092
5	5.97	0.02	0.023	- 1.70	0.0146 0.0148

The formation of complex ions between nickel and acetate ions may be represented in general by the equilibrium

$$Ni^{++} + n\,Ac^{-} \rightleftharpoons NiAc_n^{2-n},$$

and the formation constant for the complex ion can be written as

$$(4.7)\quad K = \frac{(NiAc_n)}{(Ni^{++})(Ac^-)^n} \quad .$$

Now, according to equation (3.7),

$$(4.8)\quad E = E^{o'} + 0.059/2 \log (Ni^{++}),$$

so that, solving equation (4.7) for (Ni^{++}) and substituting,

$$(4.9)\quad E = E^{o'} + 0.059/2 \log \frac{(NiAc_n)}{K} - 0.059/2 \log (Ac^-)^n,$$

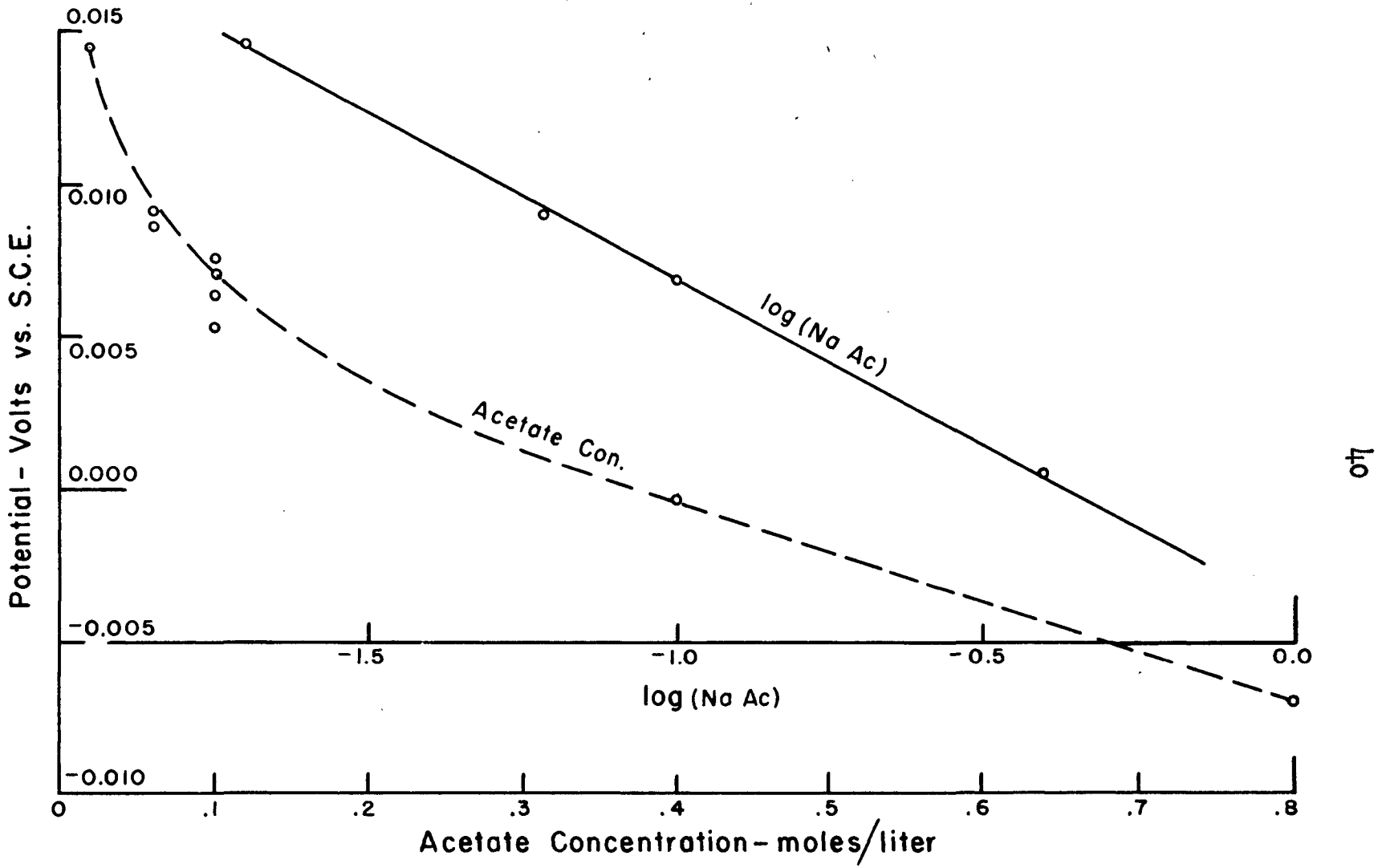
or

$$(4.10)\quad E = E^{o'} + 0.059/2 \log \frac{(NiAc_n)}{K} - n/2(0.059) \log (Ac^-).$$

In the presence of relatively large concentrations of sodium acetate $(NiAc_n)$ would be relatively constant, so that the graph of equation (4.10) should be a straight line with a slope of n/2(0.059). In Figure 8 the acetate concentration and the logarithm of the acetate concentration are plotted as a function of EMF. The graph of log (Ac^-) *vs.* EMF gives a slope of -0.011; this would require a value of n equal to approximately 1/3 if the change in EMF with sodium acetate concentration is due to complex-ion formation. Since a coordination number of 1/3 is very unlikely considering the ions involved, it appears that complex ions are not formed between nickel ion and acetate ion in the range of concentrations being studied.

The curves of Figure 7, with the exception of the 1.0 M sodium fluoride-hydrofluoric acid system, are practically superimposed one upon another. The region pNi 3 to pNi 4 appears to be linear, while the EMF reaches limiting values above and below this region.

Figure 8. Effect of sodium acetate concentration on the potential of 5,8-quinolinehydrone in 0.001 M nickel perchlorate


0.015
0.010
0.005
0.000
-0.005
-0.010
Potential - Volts vs. S.C.E.
log (Na Ac)
Acetate Con.
-1.5
-1.0
-0.5
0.0
log (Na Ac)
0
.1
.2
.3
.4
.5
.6
.7
.8
Acetate Concentration - moles/liter

The limiting value of EMF in the region above pNi 4 can be attributed to the solubility of nickel bis-5,8-quinolinediol. That is to say, the EMF approaches that value given by the buffer solution alone when saturated with nickel bis-5,8-quinolinediol.

The limiting value attained by the curves in the region below pNi 3 was thought to be due to complex-ion formation between Ni^{++} and the anion of the buffer system; however, in view of the results obtained in the preceding section, this cannot be true. Hydrolysis of Ni^{++} in the more concentrated solutions might be a possible explanation; however, Gayer and Woontner (26) determined the equilibrium constants for the hydrolysis of nickel chloride and reported a value of $K_h = 2.3 \times 10^{-11}$. There is, therefore, practically no hydrolysis of nickel ion at pH 6.

While no precipitate could be observed in the 10^{-3} M nickel solutions at pH 6, it is possible that a colloidal suspension of the basic acetate of nickel is formed and is the cause of the limiting potential in the low pNi range. According to Britton (27) nickel hydroxide does not begin to precipitate from dilute solutions until pH 6.7; however, the precipitation of basic salts frequently precedes the precipitation of the hydroxide as the pH of the solutions is raised and, further, these are often present in the form of invisible colloidal precipitates. No information could be found concerning the pH at which the basic acetate or basic salts of nickel are formed.

The general slope of the EMF-pNi curve suggests that equation (3.7) might be tested experimentally in the range pNi 3 to pNi 4. Accordingly, a series of standard nickel perchlorate solutions of ionic strength 0.10 and covering the range pNi 2.8 to pNi 4.4 in tenths of a pNi unit were prepared. The solutions were buffered with sodium acetate-acetic acid buffer at pH 5.95.

Solutions for measurement were prepared by measuring the appropriate volume of standard 0.010 M nickel perchlorate solution from a burette. A volume of 25.0 ml. of stock buffer solution (NaAc, 1.0 M; HAc, 0.05 M) was added from a pipette, and the resulting solution diluted to 250 ml. with deionized, distilled water.

The solutions were placed in the cells, brought to 25 $\pm$ 0.01° in the constant temperature bath, and nitrogen was passed through the solutions for a period of 45 minutes. A small amount (1 to 2 mg.) of nickel bis-5,8-quinolinediol and a like amount of 5,8-quinolinehydrone were added through a small opening in the top of the cell. The potential was measured as previously described. From two to five independent measurements were made on each solution. The results are listed in Table 8 and are shown graphically in Figure 9.

The most probable values of the slope and y-intercept of the line in Figure 9 were determined by the method of least squares. The intercept a and slope b of the equation of a line

$$y = a + bx$$

were calculated from the following equations (28):

Table 8. The potentials of 5,8-quinolinedione-5,8-quinolinediol in nickel perchlorate solutions buffered with sodium acetate-acetic acid and saturated with 5,8-quinolinehydrone and with nickel bis-5,8-quinolinediol

pNi	$Ni(ClO_4)_2$	Ml. stock / 250 ml.	pH	EMF (S.C.E.) (volts)
2.80	1.58×10^{-3}	39.5	5.92	0.0112
2.80	1.58×10^{-3}	39.5	5.92	0.0097
				0.0104*
2.90	1.26×10^{-3}	31.5	5.94	0.0112
2.90	1.26×10^{-3}	31.5	5.94	0.0145
2.90	1.26×10^{-3}	31.5	5.94	0.0073
2.90	1.26×10^{-3}	31.5	5.94	0.0081
				0.0077*
3.00	1.0×10^{-3}	25.0	5.95	0.0063
3.00	1.0×10^{-3}	25.0	5.95	0.0050
3.00	1.0×10^{-3}	25.0	5.95	0.0052
3.00	1.0×10^{-3}	25.0	5.95	0.0067
				0.0058*
3.10	7.95×10^{-4}	19.8	5.95	0.0034
3.10	7.95×10^{-4}	19.8	5.95	0.0036
				0.0035*
3.22	6.0×10^{-4}	15.00	5.95	- 0.0016
3.22	6.0×10^{-4}	15.00	5.95	- 0.0013
3.22	6.0×10^{-4}	15.00	5.95	- 0.0043
3.22	6.0×10^{-4}	15.00	5.95	- 0.0041
3.22	6.0×10^{-4}	15.00	5.95	0.0008
3.22	6.0×10^{-4}	15.00	5.95	0.0006
				0.0007*
3.30	5.01×10^{-4}	12.5	5.95	- 0.0028
3.30	5.01×10^{-4}	12.5	5.95	- 0.0028

*Average potential for a given pNi value.

Table 8 (Continued)

pNi	$Ni(ClO_4)_2$	Ml. stock / 250 ml.	pH	EMF (S.C.E.) (volts)
3.40	3.98×10^{-4}	9.95	5.95	- 0.0086
3.40	3.98×10^{-4}	9.95	5.95	- 0.0081
3.4	3.98×10^{-4}	9.95	5.95	- 0.0061
3.4	3.98×10^{-4}	9.95	5.95	- 0.0069
				- 0.0074*
3.50	3.16×10^{-4}	7.90	5.90	- 0.0087
3.50	3.16×10^{-4}	7.90	5.90	- 0.0080
				- 0.0084*
3.60	2.51×10^{-4}	6.25	5.92	- 0.0112
3.60	2.51×10^{-4}	6.25	5.92	- 0.0107
				- 0.0110*
3.70	2.0×10^{-4}	5.00	5.95	- 0.0160
3.70	2.0×10^{-4}	5.00	5.95	- 0.0157
				- 0.0158*
3.80	1.58×10^{-4}	3.95	5.95	- 0.0185
3.80	1.58×10^{-4}	3.95	5.95	- 0.0186
				- 0.0186*
3.90	1.26×10^{-4}	3.15	5.95	- 0.0241
3.90	1.26×10^{-4}	3.15	5.95	- 0.0215
3.90	1.26×10^{-4}	3.15	5.95	- 0.0201
3.90	1.26×10^{-4}	3.15	5.95	- 0.0213
				- 0.0218*
4.00	1.0×10^{-4}	2.50	5.95	- 0.0241
4.00	1.0×10^{-4}	2.50	5.95	- 0.0248
4.00	1.0×10^{-4}	2.50	5.95	- 0.0259
4.00	1.0×10^{-4}	2.50	5.95	- 0.0239
4.00	1.0×10^{-4}	2.50	5.95	- 0.0234
				- 0.0244*

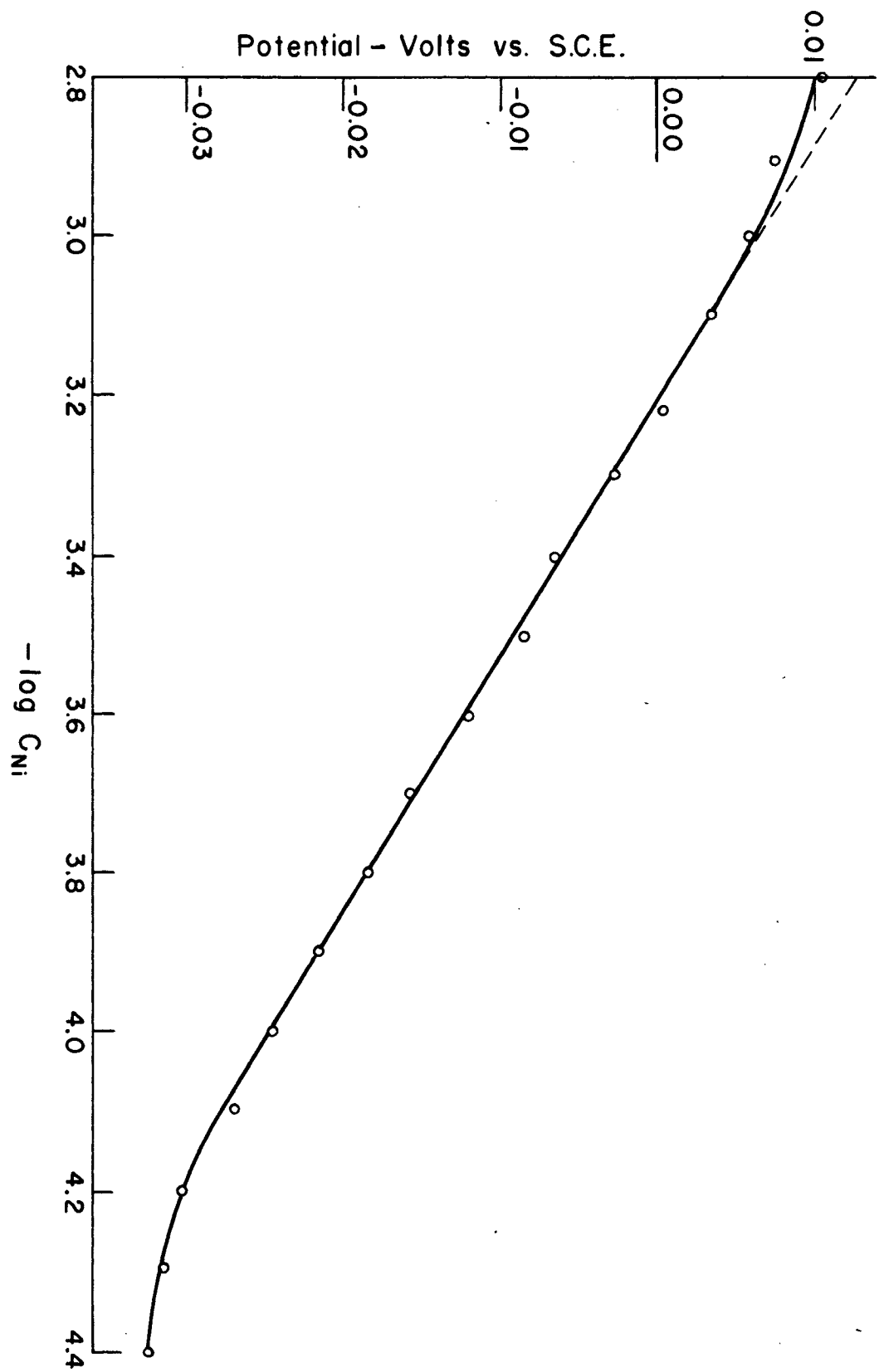
*Average potential for a given pNi value.

Table 8 (Continued)

pNi	$Ni(ClO_4)_2$	Ml. stock / 250 ml.	pH	EMF (S.C.E.) (volts)
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0235
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0268
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0283
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0294
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0274
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0262
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0272
4.10	7.95×10^{-5}	19.9/10	5.94	- 0.0280
				- 0.0272*
4.20	6.3×10^{-5}	15.8/10	5.94	- 0.0330
4.20	6.3×10^{-5}	15.8/10	5.94	- 0.0313
4.20	6.3×10^{-5}	15.8/10	5.94	- 0.0310
4.20	6.3×10^{-5}	15.8/10	5.94	- 0.0284
4.20	6.3×10^{-5}	15.8/10	5.94	- 0.0310
				- 0.0304*
4.30	5.02×10^{-5}	12.5/10	5.95	- 0.0319
4.30	5.02×10^{-5}	12.5/10	5.95	- 0.0308
4.30	5.02×10^{-5}	12.5/10	5.95	- 0.0324
4.30	5.02×10^{-5}	12.5/10	5.95	- 0.0315
				- 0.0316*
4.40	3.98×10^{-5}	9.95/10	5.95	- 0.0309
4.40	3.98×10^{-5}	9.95/10	5.95	- 0.0335
4.40	3.98×10^{-5}	9.95/10	5.95	- 0.0343
4.40	3.98×10^{-5}	9.95/10	5.95	- 0.0319
				- 0.0326*

*Average potential for a given pNi value.

Figure 9. Potential of 5,8-quinolinehydrone as a function of nickel ion concentration


Potential - Volts vs. S.C.E.
0.01
0.00
-0.01
-0.02
-0.03
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
- log C_{Ni}

$$(4.11)\quad a = \frac{\Sigma(x)\,\Sigma(xy) - \Sigma(x^2)\,\Sigma(y)}{[\Sigma(x)]^2 - n\Sigma(x^2)}$$

$$(4.12)\quad b = \frac{\Sigma(x)\,\Sigma(y) - \Sigma(xy)}{[\Sigma(x)]^2 - n\Sigma(x^2)} \quad ,$$

where $x = -\log C_{Ni}$, y = EMF vs. S.C.E., and n is the number of observations. The data and calculations are listed in Table 9.

Table 9. Data and calculations for the determination of slope and intercept of the line defined by the points given in Table 8 by the method of least squares

No. obs.	EMF	$-\log C_{Ni}$	$(-\log C_{Ni})^2$	EMF $(-\log C_{Ni})$ x 10^2
1	0.0058	3.00	9.00	1.74
2	0.0035	3.10	9.61	1.08
3	0.0007	3.22	10.4	0.225
4	- 0.0028	3.30	10.9	- 0.925
5	- 0.0074	3.40	11.6	- 2.52
6	- 0.0084	3.50	12.3	- 2.94
7	- 0.0110	3.60	13.0	- 3.96
8	- 0.0158	3.70	13.7	- 5.85
9	- 0.0186	3.80	14.4	- 7.07
10	- 0.0218	3.90	15.2	- 8.50
11	- 0.0244	4.00	16.0	- 9.76
12	- 0.0272	4.10	16.8	-11.20
13	- 0.0304	4.20	17.6	-12.80
Total	- 0.1578	46.82	170.5	-62.48

Table 9 (Continued)

Calculations for above data

$$a = \frac{\Sigma(x)\,\Sigma(xy) - \Sigma(x^2)\,\Sigma(y)}{[\Sigma(x)]^2 - n\Sigma(x^2)}$$

$$a = \frac{-(46.82)(0.6248) - (170.5)(-0.1578)}{2{,}196 - 13(170.5)}$$

$$a = + 0.098$$

$$b = \frac{\Sigma(x)\,\Sigma(y) - n\,(xy)}{[\Sigma(x)]^2 - n\Sigma(x^2)}$$

$$b = \frac{(46.82)(-0.1578) - 13(-0.6248)}{2{,}196 - 13(170.5)}$$

$$b = - 0.0306$$

4. Discussion

It has been shown by experiment that the potential of the electrode system, $Q + 2\,H^+ + 2\,e^- = H_2Q$, in a buffered solution containing nickel ion is a function of the (Ni^{++}). The dependence of EMF upon (Ni^{++}) in the range 10^{-2} to 10^{-7} M has been investigated. It has been found that the EMF of the system approaches limits at both extremes of this range of nickel concentration; the lower limit has been shown by measurements of the EMF of the system in the buffer alone, in the absence of nickel, to be due to the solubility of nickel bis-5,8-quinolinediol; it is suggested that the upper limit is due to the precipitation of basic nickel salts.

The range of nickel concentration between these two limits shows a linear relation between -log C_{Ni} and EMF. The line obtained experimentally has a slope of -0.0306, in good agreement with the value -0.0295 predicted by equation (3.7).

D. The Solubility of Nickel bis-5,8-Quinolinediol and 5,8-Quinolinehydrone at 25°

1. Nickel bis-5,8-quinolinediol

Nickel bis-5,8-quinolinediol was prepared as described in Section IV-A, except that the material of this experiment was not dried before use.

Two 125-ml. portions of the sodium acetate (0.10 M)-acetic acid (0.005 M) buffer, pH 6, were freed of oxygen by allowing a stream of nitrogen to pass through the solution for two hours. A small amount of the freshly precipitated nickel bis-5,8-quinolinediol, which had been washed four times with water, was introduced without exposing the system to air. The solution and precipitate were allowed to equilibrate for 22 hours in a constant temperature bath at 25° ± 0.01°. A slow stream of nitrogen was passed through during the equilibration period to stir the solution. The system was filtered through a porous bottom filtering crucible (#10 porosity), while the solution in contact with the precipitate was maintained in a nitrogen atmosphere.

The pH of the filtrate was carefully measured with the Beckman Model G pH Meter which had been standardized with Beckman Buffer 3506, pH 4.00.

Samples of each filtrate, 100 ml. in volume, were taken for nickel analyses. The samples were digested with nitric acid and perchloric acid to destroy organic material, taken to dryness and leached with a few drops of nitric acid and water. The resulting solutions were analyzed for nickel colorimetrically by the method of Nielsch (29), which is based on the extraction of nickel dimethylglyoxime into chloroform for spectrophotometric measurement.

A calibration curve was prepared from standard nickel solutions. These, in turn, were prepared from a stock solution containing 0.01171 mg. of nickel per milliliter as nickel perchlorate. The absorbancy was measured against a reagent blank with the Beckman Model DU Spectrophotometer at 350 mμ. The data are summarized in Table 10, and the standard curve is shown in Figure 10.

Table 10. Absorbances of some solutions of nickel dimethylglyoxime in chloroform at 350 mμ

Sample no.	Ml. stock	$(Ni)_{CHCl_3}$ (mg./25 ml.)	log I^o/I
1	5.0	0.058	0.125
2	10.0	0.117	0.261
3	15.0	0.176	0.444
4	20.0	0.234	0.521
5	25.0	0.283	0.632
#1		0.24	0.544
#2		0.21	0.468

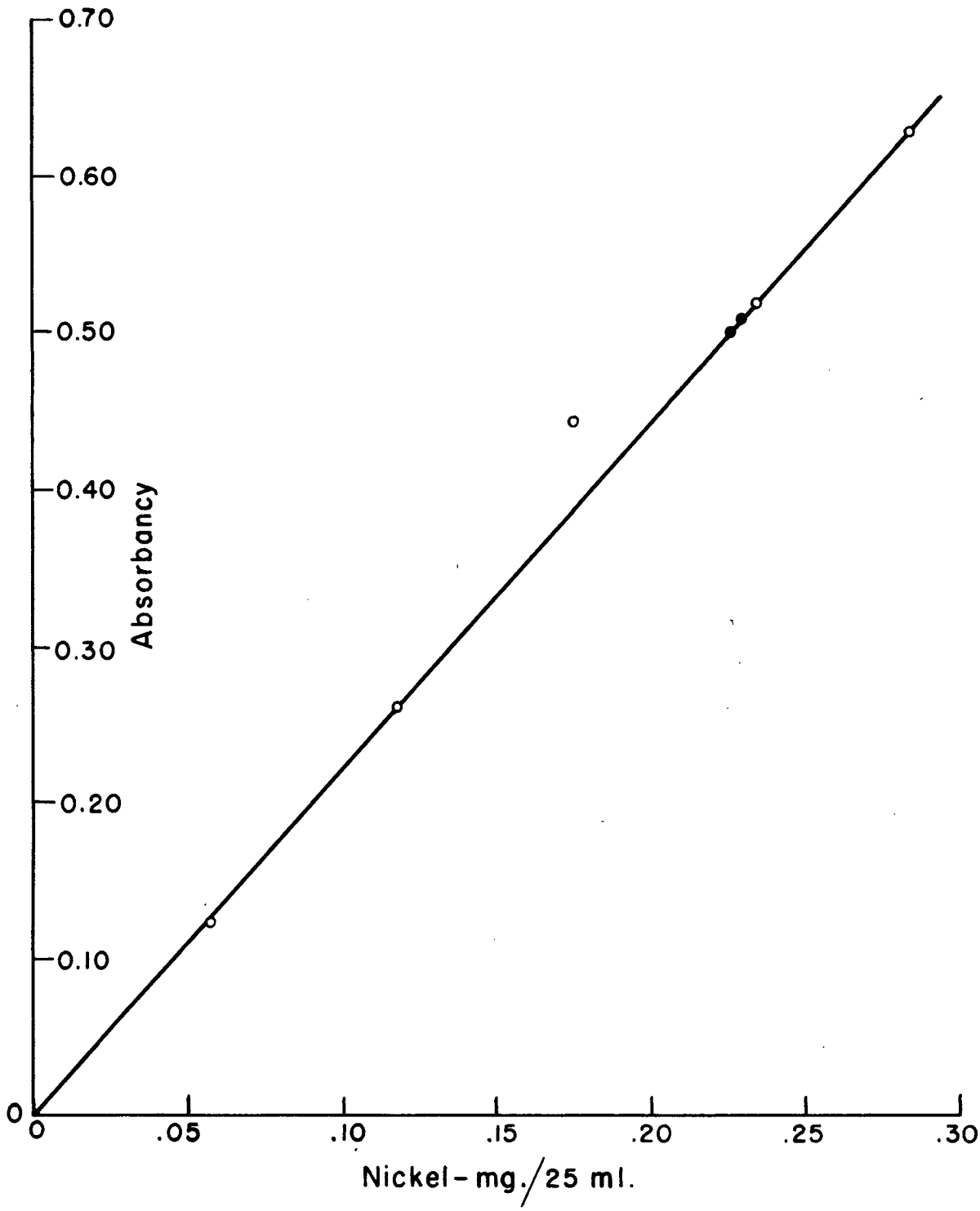


Figure 10. Colorimetric calibration curve for nickel dimethylglyoxime in chloroform at 350 mμ , ● representing standard solution and ○ representing sample solution

The calculation of results is as follows.

Sample #1	Sample #2
A = 0.544	A = 0.468
$C_{Ni}(CHCl_3)$ = 0.24 mg./25 ml.	$C_{Ni}(CHCl_3)$ = 0.21 mg./25 ml.
C_{Ni} (aq) = 2.4×10^{-3} mg./ml.	C_{Ni} (aq) = 2.1×10^{-3} mg./ml.
C_{Ni} (aq) = 4.1×10^{-5} M	C_{Ni} (aq) = 3.6×10^{-5} M
pH = 5.94	pH = 5.94

Average solubility: $3.8 \pm 0.2 \times 10^{-5}$ moles/liter

K_1 as defined in equation (3.2) may now be calculated from the above data as follows:

$$K_1 = \frac{4(Ni^{++})^3}{(H^+)^2} = \frac{4(3.8 \times 10^{-5})^3}{(1.15 \times 10^{-6})^2}$$

$$K_1 = 0.16$$

2. 5,8-Quinolinehydrone

The 5,8-quinolinehydrone for this study was prepared as described in Section IV-A. The material was recrystallized from an ether-petroleum ether mixture and obtained in the form of large black needles.

Two 75-ml. portions of sodium acetate(0.10 M)-acetic acid(.005 M) were freed of oxygen by passing a stream of nitrogen through them, 5,8-quinolinehydrone was added and the system allowed to equilibrate at 25° ± 0.01°. Aliquots were removed at regular intervals from each solution, filtered through a fine paper and the filtrate analyzed polarographically.

The polarograms of 5,8-quinolinedione and 5,8-quinolinehydrone in 0.10 M sodium acetate-0.005 M acetic acid are shown in Figures 11 and 12, respectively. The half-wave potential for the reduction wave of 5,8-quinolinedione is -0.085 ± .005 volts vs. S.C.E. A standard calibration curve was prepared by obtaining the polarograms of five standard 5,8-quinolinedione solutions and plotting the diffusion current, i_d against concentration of 5,8-quinolinedione. The standard solutions were prepared from a stock solution containing 39.70 mg. 5,8-quinolinedione/250 ml., 0.001 M. The data are given in Table 11, and the calibration curve is shown in Figure 13.

Table 11. The diffusion currents of some solutions of 5,8-quinolinedione in sodium acetate-acetic acid buffer

Soln.	(Q) moles/liter	Ml. stock/250 ml.	i_d (μa)
1	1.0×10^{-3}	Stock	4.38
2	5.0×10^{-4}	50/100 ml.	2.43
3	2.5×10^{-4}	25/100 ml.	1.25
4	1.0×10^{-4}	25/250 ml.	0.602
5	5.0×10^{-5}	5/100 ml.	0.305

The polarogram of 5,8-quinolinehydrone shows a wave which is half anodic and half cathodic.[a] The lower half of the wave corresponds to the oxidation of 5,8-quinolinediol, while the upper half of the wave corresponds to the reduction of 5,8-quinolinedione. For this reason

[a]See Otto Miller. J. Am. Chem. Soc. Vol. 62. 1940. p. 2434.

Figure 11. Polarogram of 5,8-quinolinediones in sodium acetate (0.10 M)-acetic acid (0.005 M) buffer at pH 6. Reproduced from the original tracing of the automatic recording polarograph.

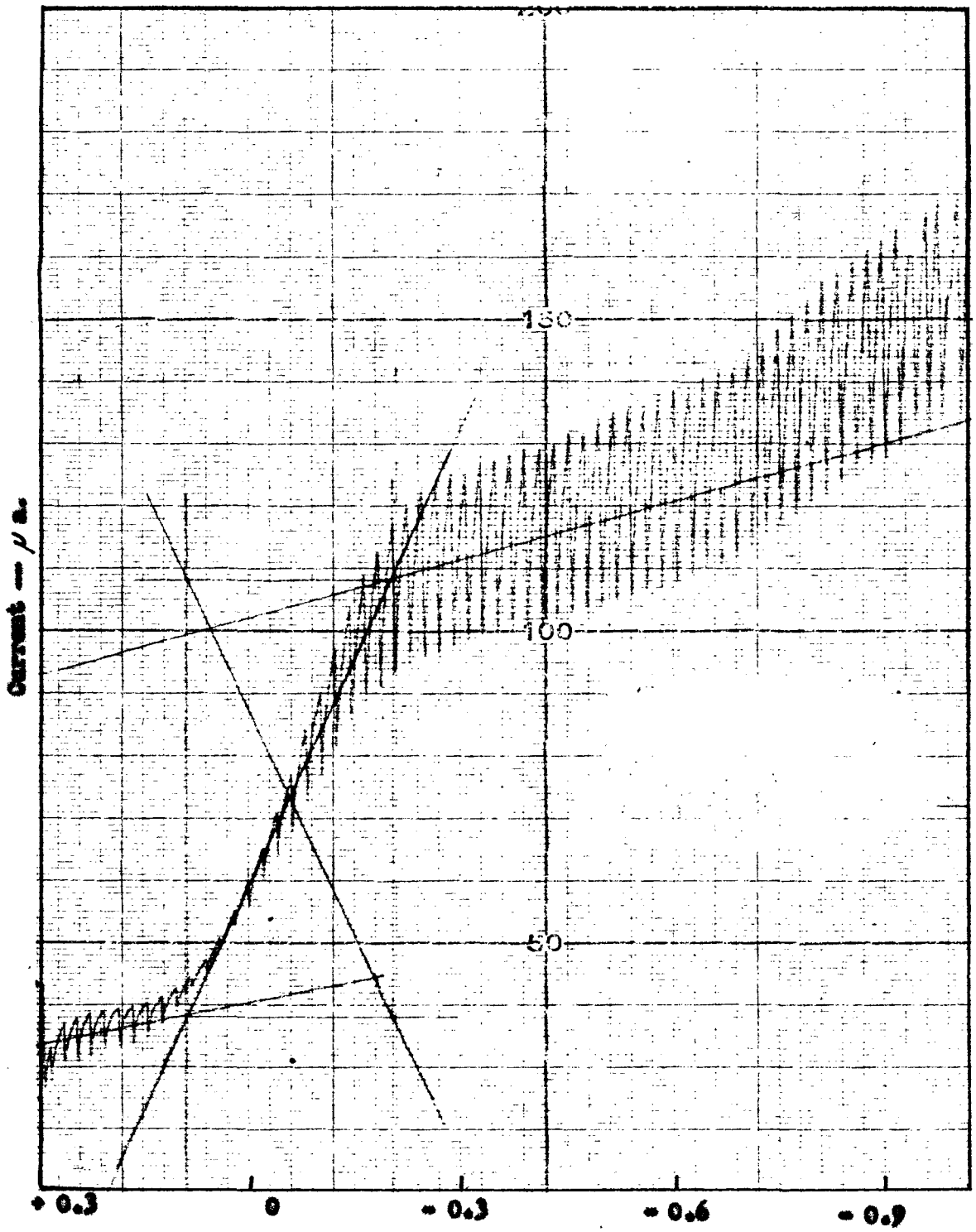
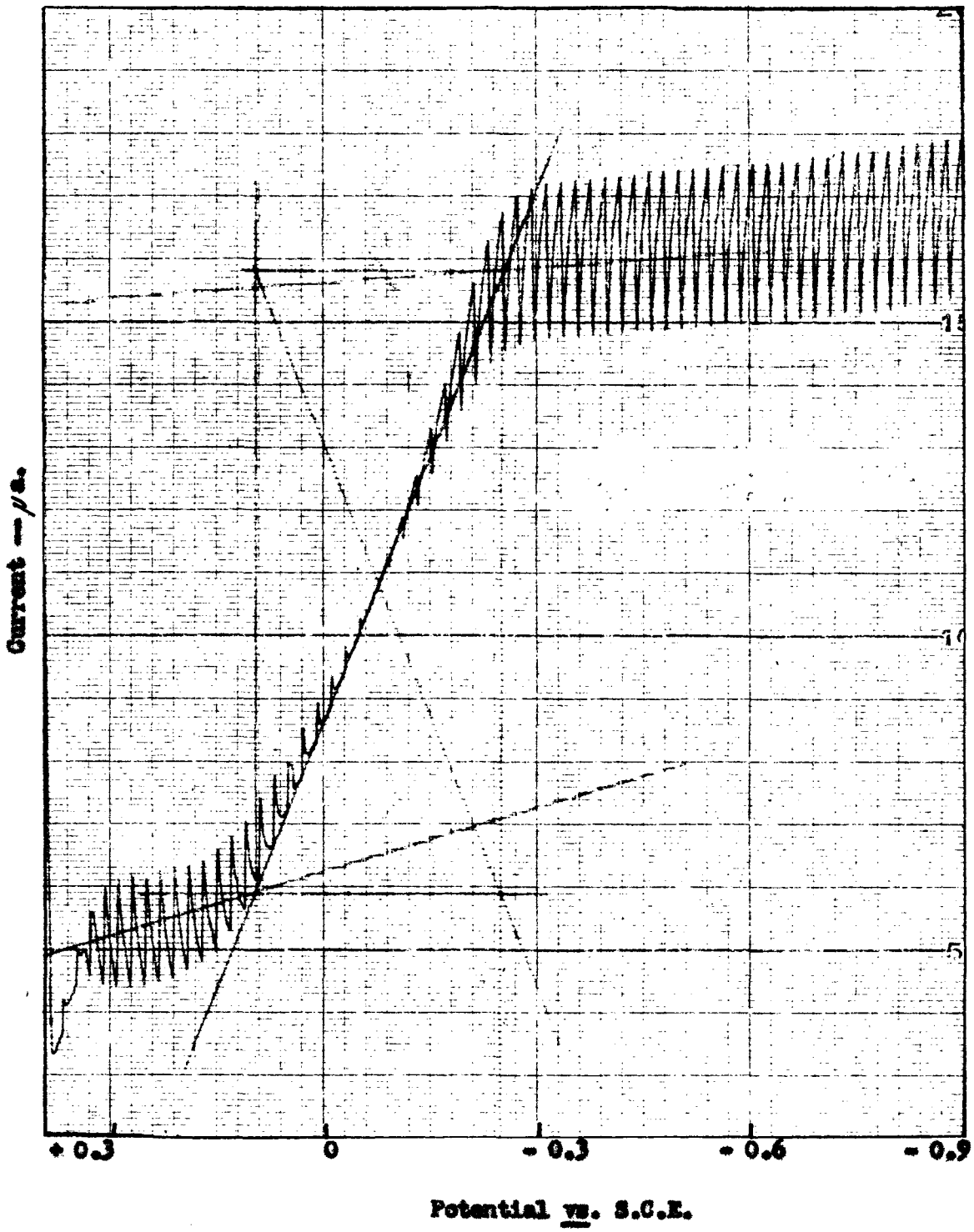

150
100
50
Current — μ a.
+ 0.3
0
- 0.3
- 0.6
- 0.9
Volts vs. S.C.E.

Figure 12. Polarogram of 5,8-quinolinehydrone in sodium acetate (0.10 M)-acetic acid (0.005 M) buffer at pH 6. Reproduced from the original tracing of the automatic-recording polarograph.


Current — μa.
+ 0.3
0
- 0.3
- 0.6
- 0.9
Potential vs. S.C.E.

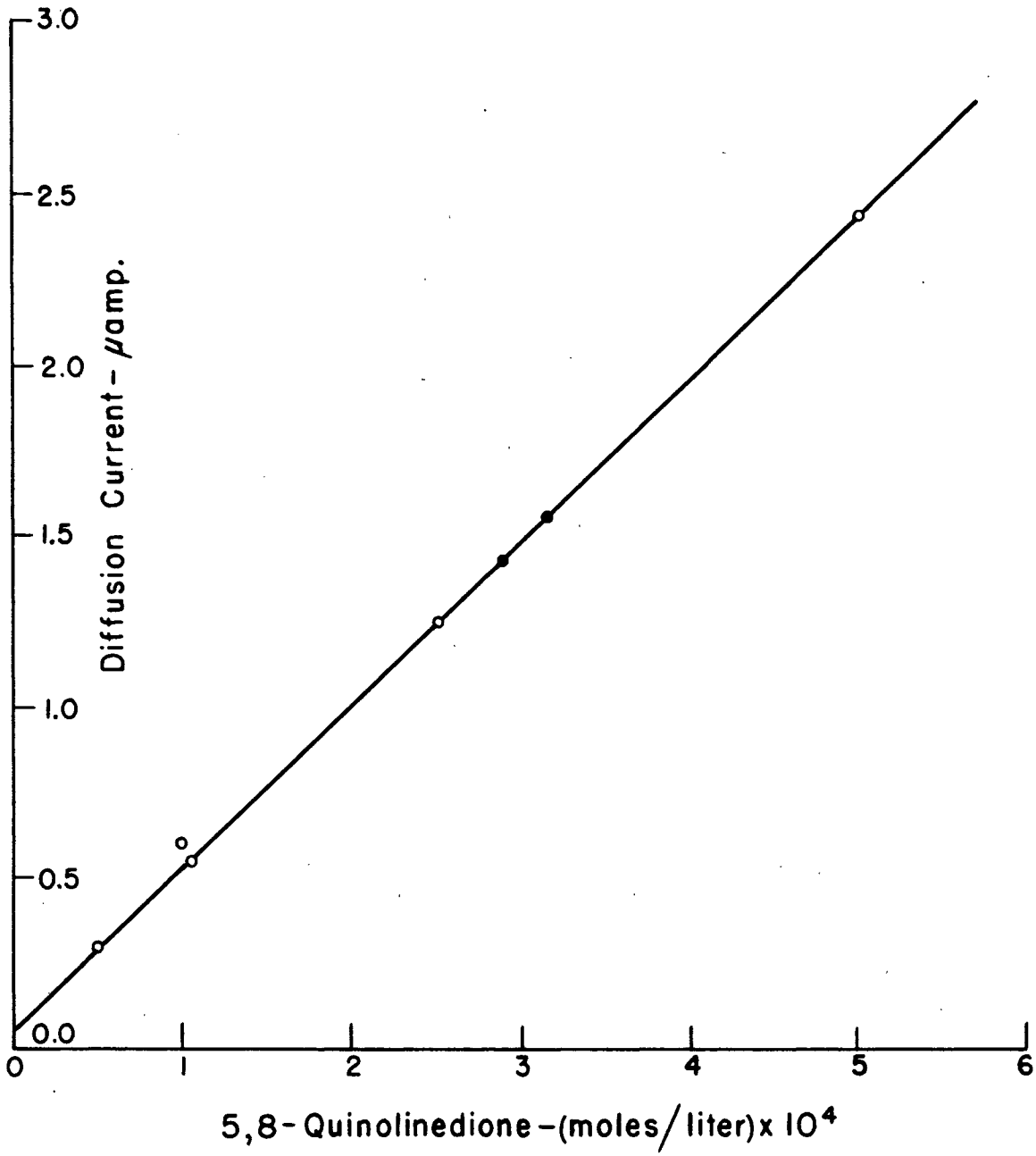


Figure 13. Calibration curve for 5,8-quinolinedione in sodium acetate (0.1 M)-acetic acid (0.005 M) buffer at pH 6, o representing standard solution and e representing sample solution

the values of i_d reported in Table 12 are equal to one half the step height of the polarographic waves. The data for successive aliquots of the equilibrated solutions are listed below.

Sample #1	Sample #2
(a) 1.48 μa	(a) 1.40 μa
(b) 1.68 μa	(b) 1.37 μa
(c) 2.88 μa	(c) 3.6 μa
(d) 1.56 μa	(d) 1.56 μa
Ave. (a, b, d) 1.57 a	Ave. (a, b, d) 1.44 a
(Q) 3.15×10^{-4}	(Q) 2.90×10^{-4}

Average (#1, #2) 3.02×10^{-4} moles per liter

E. The Calculation of the Term $E^{o'}$ of Equation 3.7

It is now possible to calculate the ratio K_2/K_1 as defined in equations (3.2) and (3.6), and by combining the value of this ratio with that of E^o_2 as determined in Section IV-B to obtain a value of $E^{o'} = E^o_2 + \frac{.0591}{2} \log K_2/K_1$.

From the solubility of 5,8-quinolinehydrone as determined in Section IV-D, one calculates K_2 as follows:

$$K_2 = (Q)(H_2Q) = S^2 ,$$

where S is the molar solubility of 5,8-quinolinehydrone.

$$K_2 = (3.02 \times 10^{-4})^2$$

$$K_2 = 9.10 \times 10^{-8}$$

Combining K_2, K_1 and E^o_2 as indicated above, one obtains

$$E^{o'} = + 0.281 + \frac{0.0591}{2} \log \frac{9.1 \times 10^{-8}}{0.16}$$

$$E^{o'} = + 0.281 + \frac{0.0591}{2} \log 5.7 \times 10^{-7}$$

$$E^{o'} = + 0.281 - 0.184$$

$$E^{o'} = + 0.097 \text{ volts} .$$

This is to be compared with the value of + 0.098 volts determined experimentally and calculated by the method of least squares in Section IV-B. The greatest uncertainty in the value of $E^{o'}$ as calculated from K_1, K_2 and E^o_2 probably lies in the determination of K_1 from the solubility of nickel bis-5,8-quinolinediol. Substitution of the lower value, 3.8×10^{-5} M, for this solubility gives a value of 0.098 volts, or an uncertainty of one millivolt in the measurement of $E^{o'}$.

If activity coefficients are taken into consideration in the calculation of K_1,

$$K_1 = \frac{(Ni^{++})(H_2Q)^2 f^{\pm}}{(H^+)^2} ,$$

where $f^{\pm}$ is the mean activity coefficient of nickel perchlorate, and the activity coefficient for the uncharged species H_2Q has been taken to be unity. Using the value 0.4 of Table 4 for the activity coefficient of nickel ion at an ionic strength of 0.10, one calculates for K_1':

$$K_1' = (0.16)(0.40) = 0.064.$$

Assuming the activity coefficient of the uncharged species H_2Q and Q to be unity, there is no change in value of K_2 on the activity basis. Recalculating $E^{o'}$ using the value of K_1' obtained above, there results

$$E^{o'}_a = 0.108 \text{ volts} .$$

F. Applications and Interference

1. Potentiometric titration of nickel with ethylenediaminetetracetic acid (EDTA)

An attempt was made to titrate a solution of nickel perchlorate (0.001 M) with 0.01 N EDTA solution, while the course of the titration was followed potentiometrically with the indicator system described in this work.

A volume of 35 ml. of 0.001 M nickel perchlorate buffered at pH 6 with a sodium acetate-acetic acid system was titrated with 0.01 N EDTA solution in the same buffer at pH 6. The potential was measured with a Pt-S.C.E. electrode system in the usual manner after each addition. No change in potential beyond a slight dilution effect was observed.

In the usual procedure for the titration of nickel with EDTA a pH of eight to ten is specified; a cyanide salt is added to keep nickel hydroxide from precipitating. In view of this, it is likely that nickel is not complexed by EDTA at the pH employed in this experiment.

2. Interference

The interference of metal ions was investigated for the case of magnesium and zinc. A volume of about 35 ml. of 0.001 M nickel

perchlorate buffered with sodium acetate-acetic acid buffer at pH 6 was prepared for potential measurement as described in Section IV-B. A solution of 0.10 M magnesium chloride or 0.10 M zinc perchlorate was added in increments from a 10-ml. burette, and the potential was measured after each addition.

No variation in EMF of the 5,8-quinolinehydrone system was observed when magnesium chloride solution was added in amounts up to five ml. Steady potentials were obtained after each addition of magnesium chloride.

The addition of zinc perchlorate solution to the solution of nickel perchlorate caused the potential of the system to drift steadily in the negative voltage direction, and steady potentials could not be obtained.

Zinc appears to interfere with the operation of the 5,8-quinolinehydrone electrode at pH 6. Magnesium does not interfere under these circumstances. Sodium ion and the anions Cl^-, F^- and OAc^- do not interfere.

V. SUMMARY OF RESULTS

1. A potentiometric method for the determination of the concentration of bivalent metal ions in aqueous solutions has been devised in analogy with the potentiometric determination of pH. The method utilizes an organic material which combines the property of reversible oxidation and reduction with the property of forming chelate ring compounds with bivalent metal ions. Specifically, the method makes use of the sequence of compounds, 5,8-quinolinedione, 5,8-quinolinehydrone and 5,8-quinolinediol. The solution containing the metal in question is buffered with respect to pH, saturated with 5,8-quinolinehydrone and with the metal derivative of 5,8-quinolinediol, and the potential between platinum and saturated calomel electrodes dipping into the solution is measured. This potential is a linear function of the logarithm of the concentration of the metal ion.

2. The theory underlying the functioning of this metal ion indicating electrode has been developed.

3. The electrode has been tested on one metal, nickel, and shown to function as predicted. There are certain limitations as to the concentration range of nickel (pNi) over which it may be used.

4. The basic organic compound for this electrode, 5,8-quinolinehydrone has been synthesized and characterized by oxidimetric titration with potassium bichromate in perchloric acid solution. The compound has the theoretical, 1/1 ratio of 5,8-quinolinediol to 5,8-quinolinedione.

The polarogram of 5,8-quinolinehydrone gives further evidence of this composition, showing a wave which is half anodic and half cathodic. The identification has been confirmed by the infra-red spectrum.

5. The potential of a series of pH buffers of ionic strength 0.10 and saturated with 5,8-quinolinehydrone has been measured, and the standard reduction potential, E^0_1, for the half-reaction, $Q + 3\ H^+ + 2\ e^- \rightleftharpoons H_3Q^+$, obtained by extrapolating to pH 0. The value so obtained is + 0.662 volts.

6. The potentials of 5,8-quinolinehydrone in solutions of nickel perchlorate in the concentration range 10^{-2} to 10^{-7} molar have been measured. The system was found to give steady potentials in solutions well buffered with respect to pH. The over-all reproducibility of these measurements over the range of nickel ion concentration studied is about 0.5 millivolts.

7. The variation of potential with -log (Ni^{++}) as measured in acetic acid-sodium acetate solutions at pH 6 is linear in the range pNi 3.0 to 4.2. The slope of the line obtained when potential is plotted against -log C_{Ni} is 0.0306 in good agreement with the theoretical slope of 0.0295.

8. The solubility of nickel bis-5,8-quinolinediol has been measured at 25° in sodium acetate-acetic acid buffer at pH 5.95. The average of two measurements is $3.8 \pm 0.2 \times 10^{-5}$ moles per liter. The solubility product, $K_1 = \dfrac{(Ni^{++})(H_2Q)^2}{(H^+)^2}$, as calculated from the solubility is 0.16 moles per liter.

9. The solubility of 5,8-quinolinehydrone has been measured at 25° in a sodium acetate-acetic acid buffer at pH 5.95. The average of two results gives a value of $3.02 \pm 0.12 \times 10^{-4}$ moles per liter. The solubility product calculated from this value is $K_2 = (Q)(H_2Q) = S^2 = 9.10 \times 10^{-8}$ $(\text{moles/liter})^2$.

10. The constant term, $E^{o'} = E^{o}_2 + .0591/2 \log (K_2/K_1)$, for the equation

$$E = E^{o'} + .0591/2 \log (Ni^{++})$$

has been calculated from the independant measurements of E^{o}_2, K_1 and K_2 described, and the value obtained is + 0.097 ± 0.001 volts *vs.* the saturated calomel electrode. The value obtained by extrapolating the graph of potential *vs.* $-\log C_{Ni}$ to unit concentration of nickel is + 0.098 volts, in good agreement with the calculated value.

11. It has been shown that the potential of the cell,

$$Pt;\ Ni^{++}(x\ M.\ \begin{matrix}\text{satd. } Ni(HQ)_2 \\ \text{satd. } H_2Q_2\end{matrix})\ //\ KCl\ (satd.);Hg_2Cl_2;\ Hg,$$

is related to the nickel ion activity of the solution by the equation,

$$(6.1)\quad E = E^{o'} + 0.059/2 \log (Ni^{++}) .$$

The cell reaction may be represented by the equation,

$$H_2Q_2 + Ni^{++} + 2\ Cl^{-} + 2\ Hg = Ni(HQ)_2 + Hg_2Cl_2 ,$$

where the reaction proceeds to the right when the electrode on the left of the cell above is negative and to the left when the calomel is negative.

According to the theory developed in Section III, $E^{o'}$ is defined by the equation,

$$E = E^{o}_{Q,\ H_2Q} + 0.0591/2 \log (K_2/K_1),$$

where K_2 and K_1 are the solubility products of 5,8-quinolinehydrone and nickel bis(5,8-quinolinediol), respectively. Potential measurements made on nickel perchlorate solutions buffered at pH 6 with a sodium acetate-acetic acid system show that equation (6.1) holds in the range pNi 3.0 to 4.2. Above pNi 4.2 the potential departs from the theoretical values owing to the solubility of nickel bis-5,8-quinolinediol and approaches the value obtained with the buffer system alone. Below pNi 3.0, the potential also departs from the theoretical values, perhaps because of the formation of basic nickel salts.

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