From a $HgCl_2$ solution of $10^{-5}$ mole/l. in 1 $N$ $H_2SO_4$ a volume corresponding to 10–20 $\mu$g. of Hg was mixed with 5.0 ml. of a ±0.006 g./l. dithizone carbon tetrachloride solution. After one minute shaking the density was measured at $\lambda$ 510 and 620 m$\mu$ in a Beckman spectrophotometer Model DU and the corresponding quantity of Hg estimated by means of a calibration curve. $p$-Chloromercuribenzoic acid also gives a stable dithizone complex under the circumstances described above. $p$-Chloromercuribenzoic acid was determined on the basis of its ultraviolet absorption. Characteristics are given in Table II.

TABLE II

CHARACTERISTICS FOR THE AROMATIC ABSORPTION OF $p$-CHLOROMERCURIBENZOIC ACID

| $p$H | $\lambda_{max}$, m$\mu$ | $E\lambda_{max}$, l. mole$^{-1}$ cm.$^{-1}$ |
|---|---|---|
| <2.0 | 238 | 15900 |
| >6.5 | 233 | 12700 |

$p$-Chloromercuribenzoic acid was estimated in a dilution of $10^{-5}$ mole/l. with a $p$H > 9.0 at $\lambda$ 233 m$\mu$.

**Procedure.—Solution** A.—±0.5 g. of radioactive mercuric oxide was dissolved in 3.0 ml. of 2.5 $N$ HCl; 2 $N$ NaOH (±1.0 ml.) was added to $p$H 6.6 and the solution made up to 250 ml. ($10^{-2}$ mole/l.).

**Solution B.**—±0.30 g. of $p$-chloromercuribenzoic acid was dissolved in 0.1 ml. of 2 $N$ NaOH; 0.1 $N$ HCl (±0.5 ml.) was added to $p$H 9.0 and the solution made up to 100 ml. ($10^{-2}$ mole/l.).

1.0 ml. of solution A, 8.0 ml. of $H_2O$ and 1.0 ml. of solution B were mixed in centrifuge tubes. After the desired time 1.0 ml. of 1 $N$ $H_2SO_4$ was added and the insoluble $p$-chloromercuribenzoic acid centrifuged. The clear solution ($HgCl_2$ fraction) was removed and a sample of 10.0 ml. was counted. The precipitate was washed with 9.0 ml. of $H_2O$ in 1.0 ml. of 1 $N$ $H_2SO_4$ and once more centrifuged. The clear supernatant was removed; to the precipitate two drops 2 $N$ NaOH were added and the solution was made up to 15.0 ml. ($ClHgC_6H_4CO_2H$ fraction); a sample of 10.0 ml. of this solution was counted. Every experiment was carried out in duplicate. At each temperature the experimental conditions for $t = 0$ were realized by adding 1.0 ml. of solution B to a mixture of 1.0 ml. of solution A, 8.0 ml. of $H_2O$ and 1.0 ml. of 1 $N$ $H_2SO_4$.

The concentrations of $HgCl_2$ and $ClHgC_6H_4CO_2H$ were varied by mixing different volumes of solution A (1.0–4.0 ml.), solution B (0.5–4.0 ml.) and water to a total volume of 10.0 ml.

The concentrations of solution A, the $HgCl_2$ fraction, solution B and the $ClHgC_6H_4CO_2H$ fraction were determined by the above-described methods.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAPE TOWN, CAPE TOWN]

# Electrochemical Behavior in Anhydrous Formic Acid. I. The Quinhydrone–Formic Acid Electrode as Polarographic Anode

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The polarographic investigation of anhydrous formic acid solutions was preceded by examination of the quinhydrone electrode in that solvent. The electrode was found to be reversible, reproducible and non-polarizable irrespective of whether nitrogen was used to agitate the solution or not. The electrode potential was found to be independent of the quality or concentration of quinhydrone used, to have an inappreciable salt effect and to be little influenced by the addition of small quantities of water. The formic acid analog of the saturated calomel electrode also was prepared. The potential of the quinhydrone–formic acid electrode against the saturated calomel–formic acid electrode was found to be +0.5384 ± 0.0005 volt at 25.00 ± 0.01°.

In an investigation of polarography in anhydrous formic acid in order to compare the measured half-wave potentials of the electro-reducible species, it was desirable to have an electrode of constant potential for use as anode. A quinhydrone–formic acid electrode was investigated for this purpose. A quinhydrone electrode has only once previously been reported as a polarographic anode.[1] This was in aqueous solution, and was found to undergo polarization, which was somewhat reduced by bubbling nitrogen through the solution. Because of it the electrode was discarded as unsatisfactory.

Because anhydrous formic acid slowly absorbs moisture, the non-polarizable electrode has to be one capable of rapid preparation, able to attain a reproducible potential instantaneously and able to maintain this value for at least a half-hour, the duration of an experiment. The electrode should not be significantly affected by traces of moisture, or small concentration of salts, and, furthermore, it should be such that liquid-junction potentials are minimized without the introduction of gel-salt bridges.

The quinhydrone–formic acid electrode was found to fulfil all these requirements. As formic acid exhibits reducing properties, a possibility exists that it may reduce quinone to hydroquinone, thereby altering the potential and vitiating its use as a reproducible electrode. If this were so, the potential should have depended markedly on the concentration of quinhydrone present, and such was not found to be the case. The quinhydrone electrode has been used in formic acid on two occasions in potentiometric studies of acid–base titrations[2,3]; Hammett and Dietz[2] stated that in the sodium formate solutions used, there was no evidence of any reaction between the formic acid and the quinhydrone. They maintained, however, that platinum electrodes were unsatisfactory, often showing differences of several millivolts in the same solution and recommended the use of gold electrodes. We have found, however, that platinum electrodes are entirely satisfactory. In a wide range of solutions, with divergent concentration of quinhydrone and supporting electrolyte, the maximum difference of potential observed between any two electrodes was 0.2 millivolt.

In aqueous polarography, the standard practice is to refer the half-wave potentials to the saturated

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[1] J. P. Baumberger and K. Bardwell, *Ind. Eng. Chem., Anal. Ed.*, **15**, 629 (1943).

[2] L. P. Hammett and R. N. Dietz, THIS JOURNAL, **52**, 4729 (1930).

[3] O. Tomicek and P. Vidner, *Chem. Listy*, **47**, 516 (1953).

calomel electrode. In our studies, we prepared the formic acid analog of this electrode, but it appeared to be much more sensitive to deterioration of the formic acid than the quinhydrone–formic acid electrode. We, therefore, used the latter as an anode in the polarographic cell and as we had previously measured its potential against the saturated calomel–formic acid electrode, the half-wave potentials could be calculated with respect to the latter reference standard.

## Experimental

**Materials.**—The formic acid, British Drug Houses 98–100% grade, was dried over anhydrous copper sulfate for two days with continuous agitation. It was then fractionally distilled at 25° under a pressure of 20 mm.; the condenser unit was cooled by circulating water at 4°. The first fraction, of about 10% of the original volume, was discarded. The product was further purified by fractional freezing, the resulting anhydrous formic acid freezing sharply at 8.40°, the accepted value of the freezing point. It was stored in sealed glass stoppered bottles at −10°.

Quinhydrone, British Drug Houses Analar grade, was further purified by recrystallizing twice from distilled water and drying for several days over anhydrous calcium chloride. Merck grade potassium chloride was recrystallized twice from distilled water and dried by heating at 180° for 5 hours. Anhydrous sodium formate, as supplied by British Drug Houses, was recrystallized twice from distilled water and desiccated at 135° for five hours, the final product melting at 250°. The value given by Groschuff was 253°.[4]

The mercury used was washed repeatedly in 5% nitric acid solution and distilled twice under reduced pressure.

**Apparatus.**—The platinum electrodes were prepared as described.[5] The platinum employed was in the form of bright unused foil and measured 10 mm. by 15 mm.; it was sealed into soft glass tubing and carefully annealed. The perfection of the seals was tested by suspending the electrodes in distilled water, which was then heated to boiling and finally allowed to cool to room temperature. Careful examination of the seals under a magnifying glass showed no imperfections. This care was necessitated due to imperfections in the metal–glass seals of quinhydrone electrodes being a prime reason for non-reproducible potentials. The electrodes were cleaned by immersion in cold chromic acid cleaning mixture, which was heated to 125° and allowed to cool overnight. After rinsing well with distilled water and absolute alcohol, the electrodes were placed in a stream of dry air for 20 minutes; when not in use they were stored over anhydrous calcium chloride.

The examination of the properties of the quinhydrone–formic acid electrode was accomplished by the formation of a cell of two compartments, each containing a platinum electrode dipping into identical formic acid solutions. The compartments were separated by a sintered glass disc, of diameter 1 cm. and a pore size of 5–10 μ. The conditions of the one electrode were then varied and the potential difference measured. Each compartment was furnished with an inlet capillary tube to enable nitrogen to be bubbled over the electrode thus producing stirring. Potential measurements were made on a Cambridge Slide Wire Potentiometer. The temperature of the water thermostat used throughout this investigation was maintained at 25.00 ± 0.01°.

The quinhydrone–formic acid half-cell was prepared by dipping the platinum electrode into a solution of 0.05 *M* quinhydrone and 0.25 *M* sodium formate in anhydrous formic acid. The sodium formate was included to reduce the resistance of the polarographic cell; it was preferred to the ammonium salt which is very hygroscopic.

In aqueous solution the quinhydrone electrode has been shown to be independent of the quality of quinhydrone used.[6–8] This conclusion was verified in formic acid by comparison of the electrode potentials developed using BDH Analar quinhydrone, with and without further purification. The potential difference of two such electrodes was on no occasion more than 0.1 millivolt. Further, the electrode potential was found to be independent of the concentration of quinhydrone.

As in aqueous solution,[9] the salt effect of the quinhydrone–formic acid electrode has been shown to be very small. The effect was examined by preparing a cell of two quinhydrone–formic acid electrodes and measuring their potential difference when the sodium formate concentration in one of them was increased. The measurements were repeated using potassium chloride as the added salt. The ionic conductances at infinite dilution of sodium, formate, potassium and chloride ions in formic acid are 14.6, 51.5, 17.5 and 18.3 mhos/sq. cm., respectively.[10,11] Substitution of these data in the Hendersen equation enabled the liquid junction potential between the two half-cells to be calculated and these results were found to agree with the measured potentials to about 6%. Further the potential differences, once established, decreased very slowly with time, showing the diffusion across the sintered glass boundary to be small.

In order to test the non-polarizability of the electrode, a cell of two electrodes was again formed. With nitrogen bubbling through each compartment the difference of potential was found to be 0.1 millivolt. A current of 40 μ-amperes was then passed through the cell for one hour after which no measurable difference was noticed. The above operation was then repeated without passing nitrogen through either compartment, after which the potential difference was found to be 1.5 millivolts but immediately dropped to 0.1 millivolt on agitating the solution with nitrogen. The results of this experiment were reproduced on five occasions. Further, the relationship between current flowing and voltage applied to the cell was found to be a linear function over a range of 0 to 1.4 volts, both with and without the passage of nitrogen through the solution. It was thus concluded that the electrode was reversible, reproducible and non-polarizable whether or not nitrogen was employed to agitate the solution.

Finally it was necessary to measure the potential of the quinhydrone–formic acid electrode against the saturated calomel–formic acid electrode. The latter was prepared in precisely the same way as its aqueous counterpart and the potential difference was measured at 25.00 ± 0.01°, again using a No. 4 sintered glass disc as the surface of separation. The mean of ten determinations gave the potential of the quinhydrone–formic acid electrode against the saturated calomel–formic acid electrode as +0.5384 ± 0.0005 volt.

As the effect of small quantities of water on the potential of the quinhydrone electrode may have been of importance, it was studied by the addition of 0.5% (v./v.) of distilled water to the anodic electrolyte, all other variables remaining unchanged. The potential of the quinhydrone–calomel cell was found to drop by about 0.4 mv. The dependence of the potential of the quinhydrone electrode on such quantities of water is thus shown to be small.

The polarographic investigation of anhydrous formic acid solutions has been so greatly facilitated by the institution of the quinhydrone–formic acid electrode that similar quinhydrone electrodes in other non-aqueous solvents may prove of considerable utility.

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