

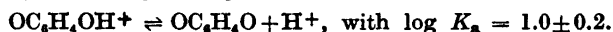
The Basicity Constant of *p*-Benzoquinone

Comparison of the Quinhydrone Half-cell with the Hydrogen Half-cell in HClO₄-NaClO₄ Ionic Medium

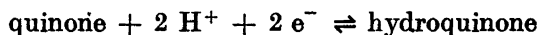
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Deviations between the quinhydrone and hydrogen half-cells at high acidities in the ionic medium HClO₄-NaClO₄ at 25°C can be interpreted by assuming the equilibrium



Investigations on cells containing quinhydrone and hydrogen electrodes¹ have established that in acid solutions of low ionic strength the quinhydrone half-cell can be considered to be equivalent to the hydrogen half-cell. This implies that under the conditions stated the electrode process



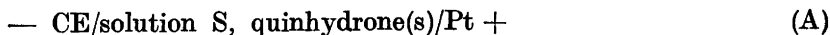
is reversible and the ratio of the activities of quinone and hydroquinone, $a_{\text{Q}}a_{\text{QH}_2}^{-1}$, is constant. As the ionic strength is increased, $\log(a_{\text{Q}}a_{\text{QH}_2}^{-1})$ is found to vary approximately linearly¹ with the concentration of the dissolved electrolytes. The dependence of the activity ratio on the composition of the solution is usually referred to as the "salt error" of the quinhydrone electrode and is explained by assuming that the dissolved substances influence differently the activity factors of quinone and hydroquinone.

Though the salt error introduces a complication, the quinhydrone electrode offers a number of advantages. It comes rapidly to equilibrium and dissolved air is without effect; in addition, the standard potential of H⁺/QH₂Q(s), Pt is +699.3 mV at 25°C¹ which makes it applicable to a number of systems which would react with H₂. On account of these features the quinhydrone half-cell has been extensively used to investigate protolytic reactions. So it was often employed to study the hydrolysis equilibria of metal ions²⁻⁷. These studies on hydrolysis were all carried out in a constant ionic medium⁸. The solutions were made to contain 1 M or 3 M ClO₄⁻ by the addition of NaClO₄, the concentration of the metal ion to be studied was kept low and the hydrogen ion concentration was varied by adding HClO₄ or NaHCO₃.

In connection with these hydrolysis studies, it was therefore of interest to compare the quinhydrone half-cell with the hydrogen half-cell and thus to ascertain whether $a_Q a_{\text{QH}_2}^{-1}$ varies as Na^+ is replaced by H^+ in the ionic media $[\text{ClO}_4^-] = 3 \text{ M}$ and 1 M .

EXPERIMENTAL RESULTS

For experimental details reference is made to previous work⁸. The emfs of the following cells were studied at 25°C



Here CE denotes the half-cell



and solution S had the general composition



h ranged from 0.0100 to 0.600 M.

The emf of cell (A) can be written at 25°C

$$E_A = E_{0A} + 59.16 \log h + 29.58 \log \left(\frac{a_Q}{a_{\text{QH}_2}} \right) + E_j \quad (1)$$

that of cell (B) at $p_{\text{H}_2} = 1 \text{ atm}$

$$E_B = E_{0B} - 59.16 \log h - E_j \quad (2)$$

where E_{0A} and E_{0B} are constants and E_j denotes the liquid junction potential between solution S and 3 M NaClO_4 . The standard state is defined so that the activity factors of the solutes approximate to unity if the solutes are present in negligible concentrations in the solvent 3 M NaClO_4 . In previous work⁸, evidence was given that f_{H^+} remains practically constant as Na^+ is replaced by H^+ up to $h = 0.6 \text{ M}$; therefore the concentration of hydrogen ions can be used in (1) and (2) instead of the activity.

If $a_Q a_{\text{QH}_2}^{-1}$ remained unchanged as h is varied, $E_A(h) + E_B(h)$ would be a constant. From the plots $E_A(h)$ and $E_B(h)$, it became apparent however that $E_A(h) + E_B(h)$, and thus $a_Q a_{\text{QH}_2}^{-1}$, decreases monotonically with h .

In order to analyze these data in more detail the function

$$\delta = \delta(h) = 29.58 \log \left(\frac{a_{\text{QH}_2}}{a_Q} \right) \quad (3)$$

is needed. To obtain δ the values of E_{0A} and E_{0B} are required. These can be found by extrapolation. When h approaches zero, E_j and δ become negligible, consequently $E_A - 59.16 \log h = E'_A$ and $E_B + 59.16 \log h = E'_B$ approach E_{0A} and E_{0B} . On plotting E'_A and E'_B against h , both functions proved to be linear up to $h = 0.250 \text{ M}$. Therefore the error involved in the extrapolations did not exceed $\pm 0.05 \text{ mV}$, which is the average uncertainty of the emf measurements.

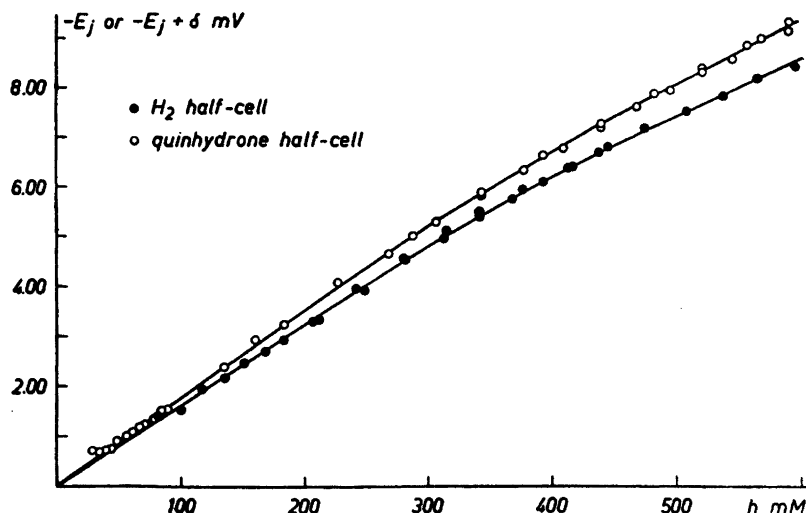


Fig. 1. $E_j - \delta$ (equation 4) and E_j (equation 5) as functions of h . The upper curve represents the equation $E_j - \delta = -59.16 \log\left(1 + \frac{2.00}{3.000} h\right) - 29.58 \log(1 + 0.1 h)$ mV. The lower curve: $E_j = -59.16 \log\left(1 + \frac{2.00}{3.000} h\right)$ mV.

Using these extrapolated E_{0A} and E_{0B} values

$$E_A - E_{0A} - 59.16 \log h = 29.58 \log \left(\frac{a_Q}{a_{QH_2}} \right) + E_j = E_j - \delta \quad (4)$$

and

$$E_{0B} - E_B - 59.16 \log h = E_j \quad (5)$$

have been computed as functions of h , these data being plotted in Fig. 1. A smooth curve has been drawn through each set of experimental points. It was found that the curve describing the measurements with the hydrogen electrode coincides within 0.10 mV with the equation

$$E_j = -59.16 \log \left(1 + \frac{2.00 h}{3.000} \right) \text{ mV} \quad (6)$$

which was found previously⁸ to give a good fit in the whole range of h studied.

With the help of these curves, δ , which is equal to (5) - (4), was read off at a number of h values. These δ values are plotted *versus* $\log h$ in Fig. 2, where the length of the vertical lines indicates the probable error.

Solutions of $[\text{ClO}_4^-] = 1 \text{ M}$ have also been studied. Measurements with silver and hydrogen half-cells have indicated that, in this ionic medium, the activity factors remain constant up to $h \sim 0.100 \text{ M}$. Therefore the measurements were not extended over $h = 0.200 \text{ M}$. A comparison of the quinhydrone half-cell with the hydrogen half-cell has shown in this case too that δ increases gradually with h ; at $h = 0.200 \text{ M}$, δ attains a value of 0.20 mV.

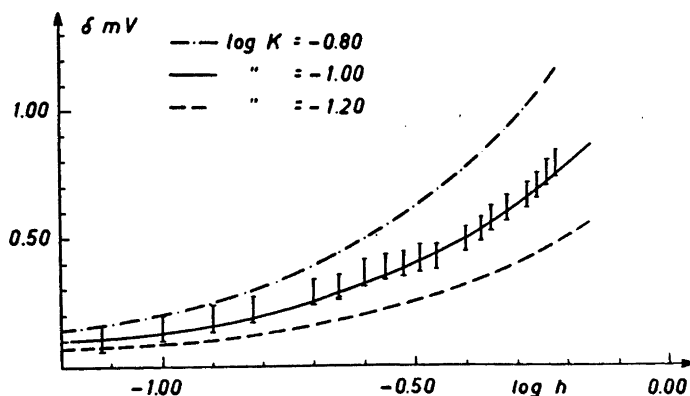


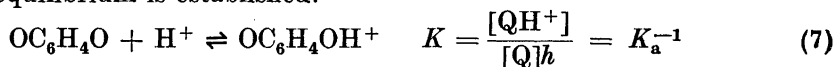
Fig. 2. δ (equation 3) as a function of $\log h$. Curves calculated with $\log K = -0.80, -1.00$ and -1.20 .

DISCUSSION

Previous measurements on the variation of $a_Q a_{QH_2}^{-1}$ have been made¹ in solutions of varying ionic strength and the results have been explained by assuming that the ratio of the activity factors of Q and QH_2 changes with the composition of the solution. This assumption does not seem to be probable in the present case, where only solutions of constant ionic strength were investigated.

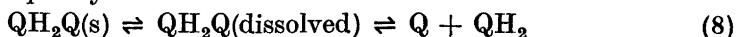
It has been shown⁸ that, in the ionic medium $[ClO_4^-] = 3$ M, the activity factors of a number of positive ions of different charge, present in concentrations which are small compared with the $[ClO_4^-]$, remain practically constant as Na^+ is replaced by H^+ up to $h = 0.600$ M. It seems reasonable to expect that the ratio of the activity factors of the two *uncharged* species, quinone and hydroquinone, which are present in small concentrations, will not change in the h range where the activity factors of positive ions remain constant.

Assuming the constancy of $f_{QH_2} f_Q^{-1}$, the experimental $\delta(h)$ data are to be explained by the variation of the *concentration* ratio $[QH_2][Q]^{-1}$. Since this ratio increases with h (see Fig. 2), the simplest assumption seems to be that quinone, as a base, reacts with H^+ forming the corresponding acid $OC_6H_4OH^+$. Thus the equilibrium is established:



The acidity constant of hydroquinone is so small, $pK_a \sim 10^{(9,10)}$, that its ionization is negligible in the h range studied.

In order to compute the equilibrium constant K , the solubility and dissociation equilibria of quinhydrone must first be considered:



According to (7) and (8)

$$[QH_2] = [Q] + [QH^+] = [Q](1 + Kh) \quad (9)$$

Thus δ , the difference between (5) and (4), will be

$$\delta = 29.58 \log (1 + Kh) \quad (10)$$

K may be conveniently calculated by comparing the experimental $\delta = \delta(\log h)$ values with the function $\delta = 29.58 \log (1 + X)$. Superimposing the experimental data on the curve $\delta(\log X)$, the difference $\log X - \log h$ gives in the position of best agreement the most probable value of $\log K$. The advantages of this graphical method for finding constants from experimental data have been outlined by Sillén¹¹. In this way it was calculated that

$$\log K = -1.0 \pm 0.2$$

As Fig. 2 shows, the agreement between the experimental data and the curve calculated with this constant may be considered satisfactory.

A great number of organic compounds containing oxygen have been found to be bases of appreciable strength, see *e.g.* Hammett¹², but of the quinones only anthraquinone has hitherto been investigated. Flexser, Hammett and Dingwall¹³ estimated, by spectrophotometric measurements, pK_a of anthraquinone to be -8.2 ± 0.2 in concentrated sulfuric acid solutions. This substance is therefore a much weaker base than *p*-benzoquinone.

This work was financially supported by *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council). I am greatly indebted to Professor Lars Gunnar Sillén for valuable criticism. I also want to thank my wife Dr. Clara Berecki-Biedermann for helpful discussions.

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Received June 26, 1956.