The Transfer Coefficient of a Redox Process at Varying pH Values as Determined by the Faradaic Rectification Method

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The periodic variation of an electrode potential about a mean potential when the electrode is polarized by a sinusoidal current is known as rectification by electrode reaction. This phenomenon, when first observed in a solution containing a redox couple, was named the "redoxokinetic effect,"[1] but it is now generally known as the Faradaic rectification.[2,3] The recent development of the Faradaic rectification allows us to study the kinetics of fast electrode processes conveniently.[4] The study can be divided into two parts. The first of them relates to the study at the mercury-aqueous solution interface by the method followed by Barker and his co-authors,[3] but corrections for the double-layer structure in the solution of the boundary-value problem and for the alternating voltage control across the Faradaic impedance at high frequencies are necessary, as has been pointed out by Matsuda and Delahay.[5] The second method previously adopted by the present author,[6] consists of studying the reaction at the platinum-aqueous solution interface, where the solution contains an equimolecular concentration of oxidant and reductant. The latter has the advantage that no correction for kinetic parameters, as suggested by Matsuda and Delahay, is necessary.

The hydrogen ion concentration of the medium used as the supporting electrolyte for the reactants has a tremendous influence on the electrode kinetics and the shift in mean potential, i. e., the redoxokinetic potential,[7] ψ; hence, the effect of pH on the transfer coefficient has been studied in the present work.

Experimental

The method for measuring a. c. voltage incident and the shift in mean potential was the same as has been described earlier.[6] The cell contained an 0.001 M solution of quinhydrone (A. R.) in a buffer solution of known pH. The pH of the buffer used varied from pH 1.4 to pH 8.1. For buffers of pH 1.4 to 4.62, sodium acetate (A. R.) and hydrochloric acid (A. R.) solutions were used; on the other hand, for buffers having pH 6.1 to pH. 8.1 solutions of disodium hydrogen phosphate (E. Merck) and potassium dihydrogen phosphate (E, Merck), the concentration of each being 1/15 M were mixed in suitable proportions to obtain a buffer of the desired pH. The exact pH of each solution was confirmed using a Leeds and Northrup pH-meter. The results obtained are given in Table I, which does not, however, include the results obtained with the buffer with pH 8.1 for want of reproducibility. For the sake of brevity, the readings of ψ obtained at 8 mV. of a. c. have not been included, as they were found to be exactly four

TABLE I. SHIFT IN MEAN POTENTIAL, ψ, AT 4 mV. OF A. C. OF THE BUFFER SOLUTIONS OF QUINHYDRONE 0.001 M IN RELATION TO THE FREQUENCY OF A. C. AND pH OF THE SOLUTIONS*,** (29±0.05°C)

Frequency c./sec.	ψ, μV. pH				
	1.40	2.10	4.62	6.10	7.10
100	34	24	18	−36	−104
200	38	34	12	−24	−53
500	38	34	4	−10	−24
1000	38	34	−1	−2	−8
2000	38	34	−1	−2	−4

* Dimensions of bright, polished platinum-foil electrodes used:

A. C. electrodes	Length cm.	Breadth cm.
1	1.6	1.0
2 (connected to the earth)	1.6	0.95
Reference electrode	1.6	1.0

** With the increase in pH, the values of ψ decrease in magnitude at the corresponding frequency. In the range of pH up to 6.1, ψ becomes constant at higher frequencies, but beyond it no such constancy is observed and the system tends to be more unstable.

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[1] K. S. G. Doss and H. P. Agarwal, *J. Sci. Ind. Res.*, **9 B**, 280 (1950).

[2] K. B. Oldham, *Trans. Faraday Soc.*, **53**, 80 (1957).

[3] G. C. Barker, R. L. Faircloth and A. W. Gardner, *Nature*, **181**, 247 (1958); G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958).

[4] H. Matsuda and P. Delahay, *J. Phys. Chem.*, **64**, 332 (1960).

[5] H. Matsuda and P. Delahay, *J. Am. Chem. Soc.*, **82**, 1547 (1960).

[6] H. P. Agarwal, *J. Electroanal. Chem.*, **5**, 236 (1963); *J. Electrochem. Soc.*, **110**, 237 (1963).

[7] H. P. Agarwal and Y. K. Gupta, *J. Sci. Soc. India*, **2**, 52 (1953).

times those shown at 4 mV. of a. c. in Table I at the corresponding frequency.

Results and Discussion

It can be seen from Table I that ψ, the shift in the mean potential, is constant at a frequency of 200 c./sec. or above when the pH of the solution is 1.4 or 2.1. Below a frequency of 200 c./sec., ψ decreases, but to confirm whether it decreases with the square root of frequency, further work at frequencies below 100 c./sec. is necessary. With the increase in the pH of the solution, ψ becomes negative; it becomes constant at a frequency of 1000 c./sec. or above (columms of pH 4.62 and pH 6.1 in Table I). With a lowering of the frequency, ψ increases in magnitude and is not proportional to the square root of frequency; therefore, the determination of the standard rate constant in such solutions is not possible. If the pH of the supporting electrolyte increases beyond 6.1, no constancy in the value of ψ is attained, even at frequency of 2000 c./sec. (column of pH 7.1 in Table I). When the pH of the medium is increased further, say, up to 8.1, the entire system becomes unstable and no reproducible observations are possible. At pH 8.1 the quinhydrone system is unstable, and so the entire solution in the cell looks black or brownish. As the constancy in the mean potential is reached at higher frequencies in the pH range of the solution from 1.4 to 6.1, the values of the transfer coefficient α, at different pH values have been calculated from the theoretical equation[8)] applicable at high frequencies:

$$\alpha = 0.5 - \frac{2\psi \boldsymbol{RT}}{V^2 n\boldsymbol{F}}$$

where ***R*** is the gas constant, *T* is the absolute temperature, *n* is the valency, ***F*** is the Faraday constant, and *V* is the a. c. voltage incident. The transfer coefficients of the quinhydrone system determined from the above equation at pH 1.4, 2.1, 4.62 and 6.1 are, respectively, 0.376, 0.389, 0.503 and 0.506 at 29°C. These results show that the transfer coefficient decreases rapidly with the lowering in the pH of the medium, but with the pH values above 4.62, the variation in the transfer coefficient is low. Further, the values of transfer coefficients lower than 0.5 indicate that, at higher hydrogen ion concentrations, the depolarising action of hydroquinone during the anodic half wave increases. When the transfer coefficient exceeds 0.5, which usually takes place at higher pH values, the conversion of quinone into hydroquinone during the cathodic half wave is favoured. Thus, the knowledge of the transfer coefficient of an electrode reaction at varying pH values helps us to understand the mechanism of electrode processes. It is interesting to note that, in buffers of higher pH values, ψ is tremendously affected in the lower frequency range.

Summary

The transfer coefficient of 0.001 M quinhydrone in buffer solutions of various pH values has been determined by Faradaic rectification studies. The value of α at 29°C has been found to be 0.376 at pH 1.4, 0.389 at pH 2.1, 0.503 at pH 4.62, and 0.506 at pH 6.1. The transfer coefficients determined at various pH values, help us to understand the mechanism of electrode processes.

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8) K. S. G. Doss and H. P. Agarwal, *Proc. Indian Acad. Sci.*, **34**, 263 (1951); ibid., **35**, 45 (1952).