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The Formal Potentials of Quinones$^{0/-}$ and Quinones$^{-/2-}$ in an Aqueous Solution

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Cyclic voltammograms of *p*-benzoquinone and its methyl derivatives are measured in a strongly alkaline aqueous solution. All of them have shown one reversible or quasi-reversible wave corresponding to the reduction of the quinones. Except for the 2,3,5,6-tetramethyl-*p*-benzoquinone (duroquinone), they have all also shown one or two additional small waves corresponding to the reduction of the OH^- adducts of the quinones. Their main waves can reasonably be explained by the calculated values of $E_1°$ and $E_2°$, which have been determined by the two-electron reduction potential and the several equilibrium constants of the quinones. The differences in the $E_1°$ and $E_2°$ values for these quiones are very small (0.007—0.046 V) in contrast to those in an aprotic solvent.

The quinone/hydroquinone (Q/QH_2) couple is known as a typical organic redox system in an aqueous solution.[1] In aprotic solvents, such as *N*,*N*-dimethylformamide (DMF) and acetonitrile (AN), the voltammograms for the reduction of *p*-benzoquinone and its methyl derivatives exhibit, respectively, two well-defined one-electron steps separated by ca. 0.6 V in the half-wave potential.[2] In an aqueous solution, however, they exhibit only one two-electron step each, the half-wave potential of which depends on the pH.[1] Such a situation as this is usually attributed to the fast protonation of the reduction products. If this is true, two one-electron waves should be observed in a highly alkaline solution, where protonation is negligible. However, this has never been realized, possibly because of the instability of these quinones in strong alkaline solutions.

This paper deals with the relation between the half-wave potentials of *p*-benzoquinone derivatives (Q) in a strongly alkaline aqueous solution and the formal potentials of $Q^{0/-}$ ($E_1°$) and $Q^{-/2-}$ ($E_2°$), which are calculated from the formal potential of Q/QH_2, the disproportionation constant of $2Q^- \rightleftarrows Q^{2-}+Q$, and the dissociation constants of QH_2 and QH^-. The $E_1°$ and $E_2°$ values may also easily be calculated from the corresponding formal potentials of protonated species, i.e., the formal potentials of Q/QH and QH/QH_2, which were calculated by Ilan et al.[3] However, their calculation makes use of the dissociation constant of QH, which is unnecessary for obtaining $E_1°$ or $E_2°$ values; this may introduce some additional errors into the resultant $E_1°$ and $E_2°$ values. Therefore, we have calculated the values of $E_1°$ and $E_2°$ directly from the original data.

Experimental

Commercial *p*-benzoquinone (BQ), 2-methyl-*p*-benzoquinone (MBQ), 2,5-dimethyl-*p*-benzoquinone (DMBQ), and 2,3,5,6-tetramethyl-*p*-benzoquinone (DQ) were purified by sublimation and recrystallization. The electrolysis cell used for cyclic voltammetry was of a three-electrode arrangement with a Mitsubishi Kasei Model 01 hanging-mercury-drop electrode (HMDE) as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. Each test solution contained 0.5 mM ($M = mol\,dm^{-3}$) of a quinone, 0.1 M of Na_2SO_4, and 0.1 M of NaOH in water. Since the quinones used were unstable in a strongly alkaline solution, a 1 M NaOH solution was added to the test solution, which was deoxygenated by bubbling with nitrogen gas, immediately before measurement. Cyclic voltammetric experiments were carried out at (20±2) °C with a scan rate of 0.1 $V\,s^{-1}$.

Results and Discussion

Calculation of $E_1°$ and $E_2°$. The following equilibria in an aqueous solution and at an electrode have been established for a quinone and its reduced species in an aqueous solution:

$$Q + e^- \rightleftharpoons Q^-; E_1° \tag{1}$$

$$Q^- + e^- \rightleftharpoons Q^{2-}; E_2° \tag{2}$$

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2; E_m° \tag{3}$$

$$2Q^- \rightleftharpoons Q + Q^{2-}; K_d \tag{4}$$

$$Q^{2-} + H^+ \rightleftharpoons QH^-; K_1 \tag{5}$$

$$QH^- + H^+ \rightleftharpoons QH_2; K_2 \tag{6}$$

where $E_m°$ is the formal potential of Eq. 3 and where the K's are the conditional equilibrium constants defined as follows:

$$K_d = [Q][Q^{2-}]/[Q^-]^2 \tag{7}$$

$$K_1 = [QH^-]/[Q^{2-}][H^+] \tag{8}$$

$$K_2 = [QH_2]/[QH^-][H^+] \tag{9}$$

Among these quantities there exist the following relations (see Appendix):

$$(E_1° + E_2°)/2 = E_m° - (RT/2F)\ln[K_1K_2(C°)^2] \tag{10}$$

and:

$$E_1° - E_2° = (RT/F)\ln K_d \tag{11}$$

Table 1. Calculated One-Electron Reduction Potentials of Quinones in Aqueous Solutions and the Literature Values for E and K Used in the Calculation [a)]

Quinone	$-E_1^\circ$/V	$-E_2^\circ$/V	$-E_m^\circ$ [b)]/V	$\log(K_1/M^{-1})$ [c)]	$\log(K_2/M^{-1})$ [c)]	$\log K_d$ [c)]
BQ	0.150	0.187	0.458	11.4	9.85	4.2
MBQ	0.215	0.233	0.412	11.5	10.05	2
DMBQ	0.304	0.350	0.352	12.5	10.35	6
DQ	0.480	0.493	0.232	13.2	11.25	1.3

a) Oxidation-reduction potentials cited refer to SCE. b) Ref. 1. c) Ref. 3.

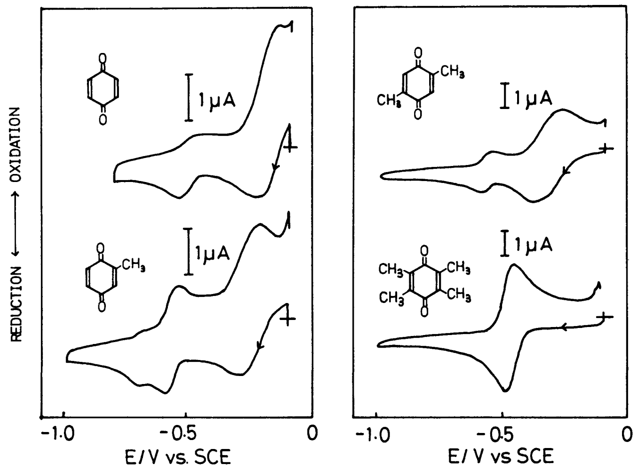
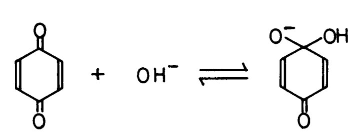


Fig. 1. Cyclic voltammograms for *p*-benzoquinone and its methyl derivatives in 0.1 M NaOH+0.1 M Li_2SO_4 aqueous solutions. Scan rate: 0.1 V s^{-1}.

where C° is the standard molar concentration: C°=1 mol dm^{-3}. Table 1 lists the E_1° and E_2° values for BQ and related substitutes calculated from these equations and also the experimental values of E_m°, K_1, K_2, and K_d used in the calculation.

Cyclic Voltammetry of *p*-Benzoquinone and Its Methyl Derivatives in a Strongly Alkaline Aqueous Solution. Figure 1 shows cyclic voltammograms for the reduction of BQ, MBQ, DMBQ, and DQ in an aqueous 0.1 M NaOH solution. These quinones give one or more quasi-reversible steps: DQ gives one; MBQ, three; and the others, two. The most positive step of each cyclic voltammogram corresponds to the redox reactions of the quinones, and the others to the redox reactions of OH^- adducts which are in equilibrium with the parent quinones, as is shown by the following equation:5)



(12)

The finding that only the cyclic voltammogram of MBQ has three steps can be explained by the fact that only the OH^- adduct of MBQ has two isomers. The cyclic voltammogram of DQ, which has only one step suggests that this compound hardly forms the OH^- adduct at all, as has been pointed out by Bishop and Tong.6)

The apparent half-wave potentials, $E_{1/2}$, determined from the midpoint of the cathodic and the anodic peak potentials of each first step are listed in Table 2, together with the peak separation, ΔE_p. The calculated values of $(E_1^\circ+E_2^\circ)/2$ and $E_1^\circ-E_2^\circ$ are also listed. Recently, Richardson and Taube7) have calculated the simulation curve for a cyclic voltammogram which has two charge-transfer steps, with various half-wave potential differences. From their results, we can calculate the apparent peak separation, ΔE_p, of the cyclic voltammogram for two-step electron-transfer reactions with small half-wave potential differences. In Table 2, the $(\Delta E_p)_{th}$ values of the quinones thus calculated by using each value of E_1° and E_2° are shown together.

The agreement between the $E_{1/2}$ and $(E_1^\circ+E_2^\circ)/2$ values is excellent. The observed values of ΔE_p are generally somewhat larger than the calculated values, $(\Delta E_p)_{th}$, but the order of the magnitude of ΔE_p and $(\Delta E_p)_{th}$ are in fair agreement with each other. The small difference between the observed and calculated values of ΔE_p may be attributed to the difference between the standard electrode potential and the half-wave potential, or the difference in the compositions of the solution with which the half-wave potential and the other equilibrium constants have been measured.

The difference between the calculated values of E_1° and E_2° are very small in contrast to those in acetonitrile, as shown in Table 2. Peover2) has measured the polarograms of several quinols in 75% ethanol containing 0.1 M NaOH as the supporting electrolyte; he has thus obtained a value of about 0.15 V as the difference between the first and second half-wave potentials. Hayano and Fujihira4) have measured polarograms of *p*-benzoquinone in DMF–ethanol mixtures and have found that the difference between the two half-wave potentials decreased from about 0.8 V in DMF to 0.15 V in ethanol. These small differences between two half-wave potentials in a protic solvent such as ethanol have been explained by these authors as the effect of hydrogen bonding between the quinone and these protic solvents. The results obtained by us in water are, therefore, not unreasonable.

From the results presented above, we can conclude that the calculated one-electron reduction potentials shown in Table 1 are reasonable as the formal potentials for Q/Q^- and Q^-/Q^{2-} in an aqueous solution, and that the first and the second one-electron reduction potentials without protonation reactions for *p*-

Table 2. Half-Wave Potentials, $E_{1/2}$, and the Peak Separations, ΔE_p, of *p*-Benzoquinone Derivatives[a)]

Quinone	In water					In acetonitrile[b)]	
	Experimental		Calculated				
	$-E_{1/2}/\mathrm{V}$	$\Delta E_p/\mathrm{V}$	$-(E_1^\circ+E_2^\circ)/2$	$(E_1^\circ-E_2^\circ)$	$(\Delta E_p)\mathrm{th}/\mathrm{V}$	$-(E_{1/2})_1/\mathrm{V}$	$-(E_{1/2})_2/\mathrm{V}$
BQ	0.172	0.095	0.169	0.037	0.059	0.51	1.14
NBQ	0.231	0.075	0.224	0.018	0.048	0.58	1.10
DMBQ	0.331	0.090	0.327	0.046	0.070	0.67	1.27
DQ	0.490	0.048	0.487	0.007	0.045	0.84	1.45

a) The potentials cited refer to SCE. b) Ref. 2.

benzoquinone and its methyl derivatives in an aqueous solution have very close values in contrast to the values of the first and the second half wave potentials of these quinones in an aprotic solvent.

Appendix

Derivation of Equation 10. $E^{\circ 1}$, $E^{\circ 2}$, K_{2a1}, and K_{2a2} in Eqs. IIa and IIIa of Ref. 3 correspond to E_1°, E_2°, $1/K_2$, and $1/K_1$ respectively in this paper. Furthermore, E_o^1 and E_o^2 in these equations are the formal potentials of the following electrode reactions:

$$Q + H^+ + e^- \rightleftharpoons QH;\ E_o^1 \qquad (A1)$$

$$QH + H^+ + e^- \rightleftharpoons QH_2;\ E_o^2 \qquad (A2)$$

From Eqs. IIa and IIIa of Ref. 3, the following equation can be obtained:

$$\begin{aligned}(E_o^1 + E_o^2)/2 &= (E^{\circ 1}+E^{\circ 2})/2 \\ &\quad - (RT/2F)\ln[K_{2a1}K_{2a2}(C^\circ)^{-2}] \qquad (A3)\end{aligned}$$

It is apparent from Eqs. A1 and A2 that $(E_o^1+E_o^2)/2$ is equal to E_m° in this paper. Therefore, using the notation of this paper, Eq. 10 is obtained:

$$(E_1^\circ + E_2^\circ)/2 = E_m^\circ + (RT/2F)\ln[K_1K_2(C^\circ)^2] \qquad (10)$$

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