

# Voltammetric determination of the $pK_a$ of various acids in polar aprotic solvents using 1,4-benzoquinone

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Dedicated to Fred C. Anson for his distinguished contributions to electrochemistry

## Abstract

The effect of various proton-donors on the electrochemical reduction of 1,4-benzoquinone (BQ) was investigated in acetonitrile, dimethylsulfoxide and methylene chloride. Three representative types of acids, protonated amines, carboxylic acids and phenol derivatives, were used as proton-donors to cover a wide range of  $pK_a$ . As a proton-donor is added, a new peak appears and the magnitude of the potential shift ( $\Delta E_p$ ) is proportional to  $-pK_a$  of the protogenic acid. Plots of  $\Delta E_p$  versus  $pK_a$  in the aprotic solvents employed in this study show good linear relationships regardless of the acid's functional group. An ECE process is believed to be responsible for this behavior and the linearity reflects dissociation of the Brønsted acid. As a consequence, it is possible to estimate the dissociation constants of various organic acids in aprotic media conveniently and reproducibly by voltammetry. A detailed interpretation of the redox behavior of quinone and some fundamental information for potentially promising analytical applications are described. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Quinone; Brønsted acids; Dissociation constants; Voltammetry; Aprotic solvents

## 1. Introduction

The acidity of a protogenic species in nonaqueous media depends on several factors such as the properties of the solvent, structure of the acid and the functional group releasing the proton [1,2]. The relative acidity in aprotic solvents may differ markedly from that in water. For instance, acetic acid ( $pK_a = 4.8$ ) is much more acidic than ammonium ion ( $pK_a = 9.2$ ) in water while the relative acidity is reversed in dimethylsulfoxide (DMSO,  $pK_a = 12.6$  for acetic acid and  $pK_a = 10.5$  for ammonium ion) [2]. The effect is even greater in acetonitrile (AN,  $pK_a = 22.3$  for acetic acid and  $pK_a = 16.5$  for ammonium ion) [2].

In order to determine the acidity of a protogenic species in nonaqueous media, several methods have been suggested and used to date. Among them, potentiometric titration, conductometry and spectrophotometry have been widely accepted and most of the dissociation constants ( $K_a$ ) of acids in the literature were obtained by these methods. Even though potentiometric titration is the most ubiquitous method up to now, it needs repeated measurements and exceptionally prudent handling because potentiometric signals from glass electrodes in nonaqueous media are not as reliable as in water, mainly due to high liquid junction potentials. Besides troublesome procedures including standardization and calibration steps, the potentiometric approach cannot be extended to high  $pK_a$  regions, as pointed out by Bordwell et al. [3]. In addition, this method requires a relatively large amount of sample and thereby has not been considered as a favorable way to determine the  $pK_a$  value of newly synthesized compounds or natural products. On the other hand, of the three methods spectrophotometry is the most preferred especially with a small amount of sample. But this

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method needs chromogenic indicators, whose absorption spectra are sensitive to the proton concentration and requires the prior knowledge of  $pK_a$  values in a given solvent [4,5]. Moreover, this method may suffer from serious error if the acid exhibits considerable chromogenic properties. Conductometry is considered inferior to the two methods mentioned above in terms of accuracy.

In addition to the conventional methods, voltammetry can be employed for the same purpose. Voltammetry has valuable advantages over other methods, such as being relatively simple and convenient, requiring only a small amount of sample for accurate measurement and covering a wide  $pK_a$  range. With regard to the voltammetric determination of  $pK_a$  in nonaqueous solvents, Sawyer and coworkers utilized the half-peak potential of proton reduction to determine the effective acidity of Brønsted acids [6]. Also Vianello and coworkers showed that the electrochemical reduction of NH-protic  $\alpha$ -bromo amide, which was used as an additive, can be utilized to determine the  $pK_a$  of weak acids in dimethylformamide (DMF) [7]. These two reports demonstrated that voltammetry is a useful technique to determine  $pK_a$  values of weak acids and also suggested that the acidity of an intermediate with a short life time can be measured by voltammetry. However complicated calculations and/or simulations for the chemical reactions involved in the electrochemical process have limited its application. In order to overcome the limitation, it is necessary to use a stable additive, whose electrochemical behavior is simple and well established. In addition, the additive must have at least one voltammetric parameter that is sensitive to the acidity and can be measured easily.

A polarographic method to determine the concentration of acids in aqueous medium through the electrochemical reduction of quinone was suggested for the first time in 1963 [8]. Based on this fundamental idea, Takamura and coworkers reported a linear relationship between  $E_{1/2}$  of methyl-*p*-benzoquinone and  $pK_a$  of several carboxylic acids and phenol derivatives in 2-methoxyethanol as well as in aqueous solution [9–11]. Similar work has been reported in DMF by Demange-Guerin [12] and by Kheifets et al. [13,14]. In these studies, only a few acids were tested to demonstrate that quinone can serve as an additive to quantify the mixed acids selectively. Also  $pK_a$  values of various weak acids were estimated on the basis of the half-wave potential ( $E_{1/2}$ ) of the new waves by dc polarography. In terms of convenience in the measurement,  $E_{1/2}$  in dc polarography, however, is not as good as the peak potential ( $E_p$ ) in linear sweep voltammetry. In addition, it should be noted that solid electrodes are more practical to use in proton-deficient nonaqueous media compared to mercury as the working electrode material. Recently, it was reported that quinone derivatives were

successfully employed to quantify the organic acids or amines and to determine the enzymatic activities by amperometry [9,15]. In spite of the well designed study, no attempt was made to determine  $pK_a$  in nonaqueous media.

In the present report, systematic evaluation of the voltammetric behavior of quinone is carried out in the presence of various proton-donors such as protonated amines, carboxylic acids and phenol derivatives in acetonitrile, dimethylsulfoxide and methylene chloride (MC), which are different in polarity and basicity. In addition, the feasibility of its practical application to determine  $pK_a$  and the solvent effect are described.

## 2. Experimental

Electrochemical experiments were performed with a Windows-driven BAS100B/W electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) using a conventional three-electrode cell, with a glassy carbon working electrode (area; 0.071 cm<sup>2</sup>), platinum wire counter electrode and Ag|Ag<sup>+</sup>|0.1 M AgNO<sub>3</sub> reference electrode, separated from the solution by a Vycor plug. The surface of the working electrode was polished with 0.3  $\mu$ m alumina (Buehler, Lake Bluff, MN), then rinsed with deionized water and washed carefully with the solvent to be used. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP). The concentration of 1,4-benzoquinone (BQ) was 0.50 mM and an appropriate amount of acid was added with a micro-syringe. All experiments were carried out under a nitrogen atmosphere and the solution temperature was maintained at 25.0  $\pm$  0.1°C by a thermostat (model B, Lauda-Königshofen, Germany).

HPLC grade AN, DMF and MC from Fisher and DMSO for spectroscopy from Merck were used as solvents. BQ was purchased from Junsei Chemical. *n*-Butylammonium perchlorate and tri-*n*-butylammonium perchlorate were synthesized from the corresponding amines and perchloric acid. Other reagents were obtained from Aldrich. Hygroscopic reagents were dried for 48 h under reduced pressure at 20°C.

## 3. Results and discussion

### 3.1. New reduction peak caused by Brønsted acids

In the proton-deficient environment, two pairs of reversible redox waves are generally observed by cyclic voltammetry of BQ [16,17]. These two reduction peaks are due to the electrochemical reduction producing a monoanion radical (BQ<sup>-•</sup>) and a dianion (BQ<sup>2-</sup>), respectively. The voltammetric behavior of BQ changes significantly when a Brønsted acid is added to the

solution. The redox behavior of BQ strongly depends on the strength of the Brønsted acid. Concerning the effect of the Brønsted acid, Gupta and Linschitz showed that weak hydrogen-bonding agents or weak Brønsted acids such as alcohols ( $pK_a > 9.3$  in aqueous media) interact with neither BQ nor  $BQ^{-\bullet}$  while  $BQ^{2-}$  associates with the acids by hydrogen-bonding [18]. According to this report, the second reduction peak producing  $BQ^{2-}$  shifted to the positive direction and the potential value varied with the concentration of the agents, whereas the first reduction peak producing  $BQ^{-\bullet}$  remained intact. The report also demonstrated that the presence of acids with medium or strong acidity commonly gave rise to a new peak prior to the first reduction peak but the mechanism was different, ECE ( $e^-H^+e^-$ ) and prior protonation, respectively. The acidity of the Brønsted acids as well as the basicity of the quinones influenced the species responsible for the new peak.

Table 1 lists the  $pK_a$  values of organic acids that have been tested in the present study. Except for some protonated alkylamines,  $pK_a$  values of all the acids are less than 9 in aqueous media. Although protonated alkylamines in Table 1 are weaker acids than carboxylic acids and phenol derivatives in aqueous media, they are comparable or stronger acids in AN and DMSO. Thus, the acids in Table 1 are regarded as intermediate Brønsted acids. In the case of strong Brønsted acids, it is expected that both the first and second reduction peaks will be affected significantly and a new reduction peak will appear at a more positive potential than that of the original peak.

Fig. 1 shows the electrochemical behavior of BQ in the absence and presence of one equivalent of *n*-butylammonium ion in AN. A new reduction peak appears at a more positive potential, around  $-0.45$  V, than the peak potential due to the first reduction of BQ alone. All of the acids in Table 1 exhibit analogous voltam-

Table 1  
 $pK_a$  and voltammetric parameters of BQ in the presence of Brønsted acids

Acids	Water	DMSO		AN		MC
	$pK_a$	$pK_a^a$	$\Delta E_p/mV^b$	$pK_a^a$	$\Delta E_p/mV^b$	$\Delta E_p/mV^b$
Sulfanilic acid	3.23	3.5 <sup>d</sup>	348		<sup>c</sup>	<sup>c</sup>
Aniline hydrochloride	4.1	3.7	332	10.56	588	<sup>c</sup>
Pyridine hydrochloride	5.2	3.5	348	12.3	528	<sup>c</sup>
Ammonium perchlorate	9.2	10.4	134	16.46	412	<sup>c</sup>
<i>n</i> -Butylammonium perchlorate	10.6	11.1	98	18.26	324	418
Tri- <i>n</i> -butylammonium perchlorate	10.9	8.4	172	18.1	324	264
Piperidine hydrochloride	11.12	10.6	108	18.92	284	308
Guanidine hydrochloride	13.54		$\sim 0$	24.5 <sup>d</sup>	24	<sup>c</sup>
Trichloroacetic acid	0.66	2.5 <sup>d</sup>	380	12.4 <sup>d</sup>	584	555
Dichloroacetic acid	1.30	6.36	258	15.81	472	<sup>c</sup>
2,4-Dinitrobenzoic acid	1.43	6.52	244	16.19	396	370
2,6-Dichlorobenzoic acid	1.6	8.7 <sup>d</sup>	176	17.6	364	<sup>c</sup>
2-Nitrobenzoic acid	2.18	8.18	184	18.24	308	280
2,6-Dihydroxybenzoic acid	2.94	3.1	368	12.6	592	571
Salicylic acid	2.97	6.8	232	16.7	398	366
3-Nitrobenzoic acid	3.4	9.2	180	19.29	260	260
1-Naphthoic acid	3.7	11.0 <sup>d</sup>	100	21.3 <sup>d</sup>	174	224
Benzoic acid	4.2	11.1	89	20.7	196	173
Acetic acid	4.8	12.3	$\sim 0$	22.31	104	163
Picric acid	0.25	-1.0	368 <sup>c</sup>	11.1	680	740
2,4-Dinitronaphthol		2.1	388	14.5 <sup>d</sup>	484	412
2,6-Dinitrophenol	3.71	4.82	312	16.0	440	<sup>c</sup>
2,4-Dinitrophenol	4.1	5.00	308	16.0	456	428
4-Nitro-3-CF <sub>3</sub> -phenol	6.4	9.33	148	19.3	264	280
4-Nitrophenol	7.15	10.8	103	20.7	188	184
2,3-Dihydroxy naphthalene		13.7	$\sim 0$	19.1 <sup>d</sup>	274	372
3-Nitrophenol	8.4	13.91	$\sim 0$	23.85	24	226
Pyrogallol	8.94		$\sim 0$	23.4 <sup>d</sup>	74	<sup>c</sup>

<sup>a</sup> From the literature [19].

<sup>b</sup>  $\Delta E_p = E_{p2} - E_{p1}$ , where  $E_{p1}$  is the peak potential of the original peak due to the first reduction of 0.50 mM BQ and  $E_{p2}$  is the peak potential of the new reduction peak of BQ in the presence of 0.50 mM acid.

<sup>c</sup> Could not be determined because of low solubility.

<sup>d</sup> Measured in this work using  $\Delta E_p$  values.

<sup>e</sup> Unusually small  $\Delta E_p$  value and has not been included in Figs. 3 and 5. See the text.

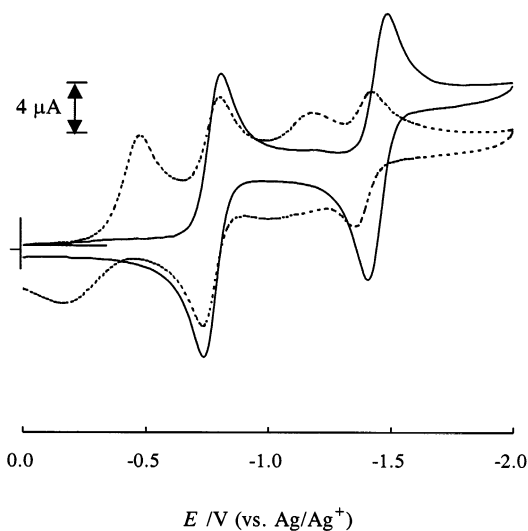


Fig. 1. Cyclic voltammograms of 0.50 mM BQ in the absence (solid line) and presence (dotted line) of n-butylammonium perchlorate in AN. Scan rate;  $50 \text{ mV s}^{-1}$ , working electrode; glassy carbon. In CV's, please note that cathodic currents are plotted positive.

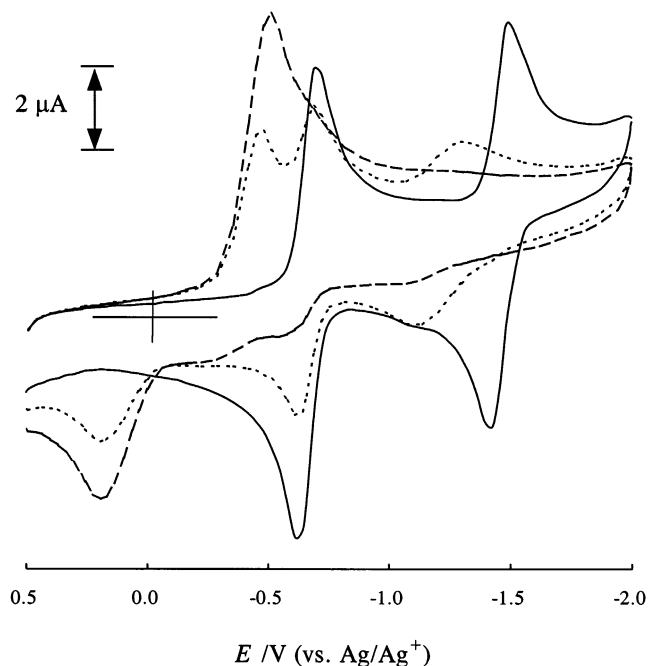


Fig. 2. Cyclic voltammograms of 0.50 mM BQ in the absence (solid line) and presence of salicylic acid in DMSO. Concentration of salicylic acid is 0.50 (dotted line) and 1.0 mM (dashed line). Other experimental conditions are the same as those in Fig. 1.

metric behavior to Fig. 1 but the individual peak potentials of the new reduction peak are different. Similar behavior is observed in DMSO and MC. In order to understand the nature of the new reduction peaks, three possible processes are examined.

Case 1: BQ becomes protonated ahead of reduction and thus the reduction peak is assigned to the reduction of  $\text{BQH}^+$ .

Case 2: BQ associates with the acid by hydrogen-bonding and the reduction peak is attributed to the reduction of acid-BQ adduct.

Case 3:  $\text{BQ}^{\cdot-}$  takes a proton from the acid and thus the second electron transfer becomes facilitated. In this case, an ECE process results where E and C refer to the electron transfer and chemical reaction, respectively.

Since  $\text{BQH}^+$  ( $\text{p}K_a = \sim -7$ ) is such a strong acid that BQ is difficult to protonate in aqueous solution, Case 1 is not reasonable. On the other hand, acids with strong hydrogen-bonding power could be combined with BQ by hydrogen-bonding. If hydrogen-bonding between  $\text{BQ}^{\cdot-}$  and acid occurs, the redox wave should gradually shift to the positive direction without altering the symmetric shape as the concentration of acid increases [18]. But the new redox waves in Fig. 1 are totally asymmetric. Moreover, Fig. 2 shows that the new peak grows with a little shift of potential as the concentration of acid increases. As a consequence, neither Case 1 nor 2 is responsible for the voltammetric behavior of Figs. 1 and 2.

The electrochemical behavior of BQ in the presence of acids presented in this study is very similar to that observed from the trifluoro acetic acid tetrachloro-1,4-benzoquinone system, which was reported by Gupta and Linschitz [18]. An ECE ( $e^- \text{H}^+ e^-$ ) mechanism suggested in the report rationalizes the effect of the acids well. The characteristic  $\Delta E_p$  depending on the  $\text{p}K_a$  of the acids in Table 1 is consistent with this interpretation. Therefore, the new reduction peak in the presence of the acids investigated in this study must be attributed to the ECE process.

The voltammetric responses in DMSO and MC are very similar to those obtained in AN.  $\Delta E_p$ s are smaller in DMSO and larger in MC than in AN for the same acid. Since DMSO is likely to interfere as a base and compete with quinone, the effect of protonation is not as great as that observed in AN and vice versa in MC. In the case of MC, its inertness and low dielectric constant are believed to facilitate the proton transfer substantially following the first electron transfer.

### 3.2. Effect of the functional group and solvent

Since the reduction mechanism of BQ involves a proton, the magnitude of  $\Delta E_p$ , the potential difference between the new peak and the original peak due to the first reduction of BQ, is suggested as a voltammetric parameter to estimate  $\text{p}K_a$  values in aprotic media. Although the redox behavior of BQ in the presence of acid is not completely understood, it turns out to be possible to use the first reduction process to simplify the situation for the practical application proposed in this study.

Fig. 3 shows the plots of  $\Delta E_p$  against  $pK_a$  obtained in aqueous media in three different aprotic solvents. As long as the acids have the same functional group, there is a linear relationship between  $\Delta E_p$  in a given solvent and the  $pK_a$  obtained in aqueous media. But acids with different groups exhibit different slopes. The  $\Delta E_p$  are in the order of protonated amines > phenols > carboxylic acids. In particular, the  $\Delta E_p$  due to protonated amines in aprotic media is abnormally large. This is not surprising, considering that protonated amines are originally

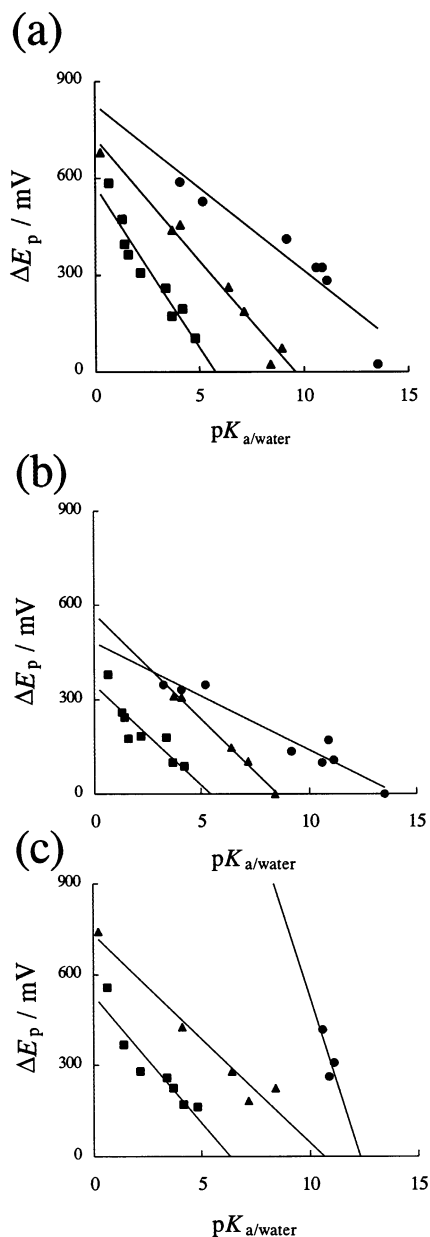


Fig. 3. Effect of  $pK_a$  on  $\Delta E_p$  in AN (a), DMSO (b) and MC (c).  $\Delta E_p = E_{p2} - E_{p1}$ , where  $E_{p1}$  and  $E_{p2}$  represent the peak potential due to the first reduction of BQ in the absence and presence of acid, respectively. Circles, rectangles and triangles denote protonated amines, carboxylic acids and phenol derivatives, respectively. All  $pK_a$  values obtained in water were from the literature [18].

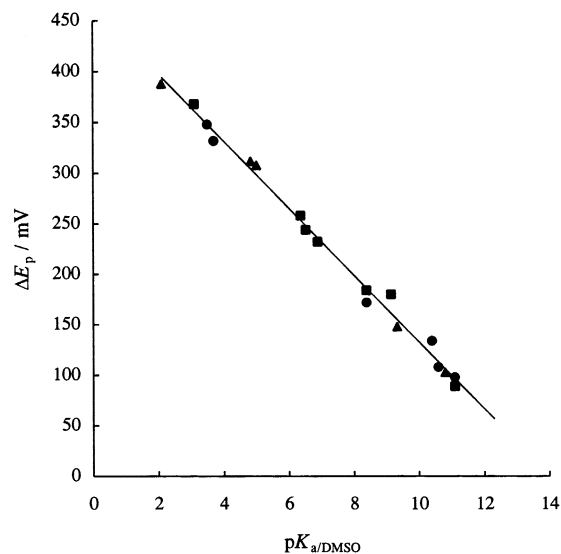


Fig. 4. Relationship between  $\Delta E_p$  and  $pK_a$  in AN. All conditions and notations are the same as those in Fig. 3.

monovalent cations, whereas carboxylic acids and phenol-type acids are neutral species. As the dielectric constant of the solvent decreases, charged species becomes unstable whereas uncharged ones are stabilized. On the other hand, a different linear relationship between  $\Delta E_p$ s and  $pK_a$  for phenol derivatives compared with that for carboxylic acids appears to be due to the stability of anions. In the case of neutral acids such as phenol derivatives and carboxylic acids, the stability of conjugate anionic bases is the key factor determining the proton-donating power of the acid because the solvation of anions needs more energy in AN, DMSO and MC than in aqueous media [20]. A negative charge on the phenolate ring is more effectively delocalized than that on the carboxylate group and is preferred in less polar media.

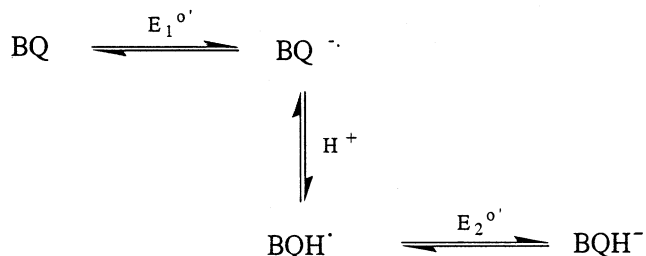
Similar results are also obtained in other aprotic solvents such as DMSO and MC. The  $\Delta E_p$  values due to the same acid in different solvents are different in the order of MC > AN > DMSO as demonstrated in Fig. 3. When the solvent is inert and its basicity is extremely small, the proton-donating power of the acids is amplified and, thus, is clearly reflected by the magnitude of  $\Delta E_p$ . Since it is more difficult to employ conventional methods in less polar solvents, this voltammetric technique seems quite useful especially when the relative proton-donating powers of various acids are compared and assessed in inert solvents.

### 3.3. Relationship between $\Delta E_p$ and $pK_a$

When  $\Delta E_p$  data are plotted against  $pK_a$  in corresponding aprotic media, good straight lines with correlation coefficients ( $R^2$ ) of 0.99 for AN and 0.97 for DMSO are observed irrespective of the functional groups of the acids as shown respectively, in Figs. 4 and 5. The slopes are

–0.046 and –0.033 V per  $pK_a$  unit in AN and DMSO, respectively. Assuming that  $\Delta E_p$  should be at least 50 mV for two adjacent peaks considered to be well separated, Figs. 4 and 5 indicate that  $pK_a$  values less than 24 in AN and 12 in DMSO can be determined by this method.

Based on the proposed ECE mechanism, the electrochemical and chemical processes in the presence of acid can be depicted as the following scheme:



In order to find out the origin of the linear relationship between  $\Delta E_p$  and  $pK_a$ , a rigorous mathematical treatment with two Nernst equations, two acid dissociation constants (acid,  $K_a$  and protonated BQ anion radical,  $K_a^Q$ ) and complicated quantitative expressions, has to be carried out. It seems unnecessary, however, to explore further in detail considering the fact that complex chemistry is involved around the electrode in an aprotic solvent. Instead, a simple derivation with two Nernst equations, acid dissociation constants and assuming  $\Delta E^{o'} \cong \Delta E_p$  and  $[\text{BQH}^-] = [\text{A}^-]$  when the initial concentrations of HA and BQ are the same provides an interesting expression:

$$E = E_1^{o'} + \frac{RT}{F} \ln \frac{[\text{BQ}]}{[\text{BQ}^{\bullet -}]} \quad (1)$$

$$E = E_2^{o'} + \frac{RT}{F} \ln \frac{[\text{BQH}^{\bullet}]}{[\text{BQH}^-]} \quad (2)$$

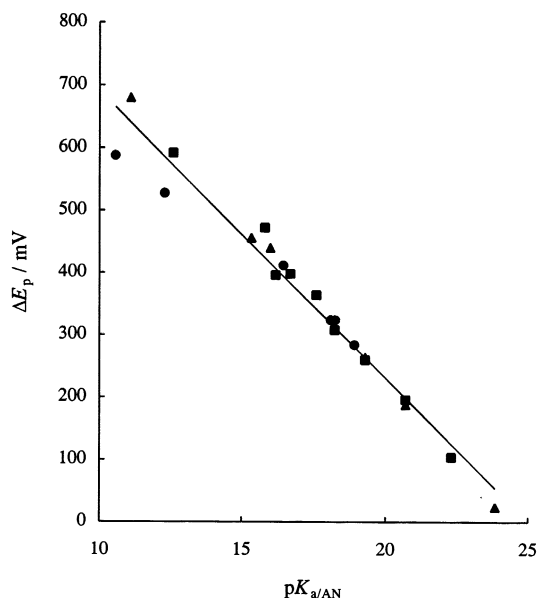


Fig. 5. Relationship between  $\Delta E_p$  and  $pK_a$  in DMSO. All conditions and notations are the same as those in Fig. 3.

$$K_a^Q = \frac{[\text{BQ}^{\bullet -}][\text{H}^+]}{[\text{BQH}^{\bullet}]} \quad K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

Adding Eqs. (1) and (2), and replacing with two acid dissociation constants gives

$$E = \frac{E_2^{o'} + E_1^{o'}}{2} + \frac{2.3RT}{2F} (pK_a^Q - pK_a) + \frac{RT}{2F} \ln \frac{[\text{BQ}]^2}{[\text{BQH}^{\bullet}]^2} \quad (3)$$

Then the potential of the new peak in the presence of acid when  $[\text{BQ}] = [\text{BQH}^-]$  (formal potential) can be written as:

$$E_{\text{new}}^{o'} = \frac{E_2^{o'} + E_1^{o'}}{2} + \frac{2.3RT(pK_a^Q - pK_a)}{2F} \quad (4)$$

while the formal potential in the absence of acid is

$$E_{\text{original}}^{o'} = E_1^{o'} \quad (5)$$

Therefore, the difference in formal potentials which is related to the potential difference between two peaks can be expressed as the following.

$$\Delta E^{o'} = E_{\text{new}}^{o'} - E_{\text{original}}^{o'} = \frac{E_2^{o'} - E_1^{o'}}{2} + \frac{2.3RT}{2F} (pK_a^Q - pK_a) \quad (6)$$

Eq. (6) indicates that the differences in the formal potentials,  $\Delta E^{o'}$ , are directly dependent on the dissociation equilibria between  $\text{BQH}^{\bullet}$  and acids.

It should be noted that serious error might be involved in the expression because of over simplified assumptions, for instance,  $[\text{BQH}^{\bullet}]$  must require more complicated terms by considering all chemical species involved in the system including prior association between BQ and the acid through hydrogen-bonding [18] especially in less polar solvents. Also, an additional error must be present by taking  $\Delta E^{o'} \cong \Delta E_p$  because the electrochemical behavior is not reversible. Nevertheless, good straight lines in Figs. 4 and 5 indicate that there is a linear relationship between  $\Delta E_p$  and  $pK_a$  with a theoretical slope of –0.030 V per decade (at 25°C) which is very close to the experimentally obtained slope of –0.033 V per decade in DMSO. It is reasonable to observe an even larger slope in AN (–0.046 V per decade) because of a strong tendency for association in AN. This comparison confirms indirectly that the interpretation based on an ECE process is reasonable to accept.

Such a high sensitivity enables us to utilize the voltammetric method to determine  $pK_a$  in DMSO and AN with good reproducibility of about 0.1 units of  $pK_a$ .  $\Delta E_p$  data in Table 1 are used to determine the  $pK_a$  of several acids including trichloroacetic acid and 1-naphthoic acid which have not been reported in DMSO and AN so far. They are listed in Table 1. Consequently,  $\Delta E_p$  measured by voltammetry is a good parameter to evaluate  $pK_a$  in aprotic solvent in terms of accuracy, convenience and the amount of sample that needs to be

prepared. In addition, this method is useful in a variety of aprotic solvents.

#### 4. Conclusions

The voltammetric response of 1,4-benzoquinone in the presence of Brønsted acids with various acid functional groups was studied in acetonitrile, dimethylsulfoxide and methylene chloride. The magnitude of the potential shift caused by the presence of the acid showed a good linear relationship with the acid dissociation constants,  $pK_a$ , in the corresponding media. The  $pK_a$  value of organic acids in aprotic solvents, therefore, can be determined based on the voltammetric behavior of quinone, which is very sensitive to the acidity of proton sources. The method proposed in this study is quite useful to assess the relative proton-donating power in non-polar aprotic media, especially when no conventional method can be used to measure the  $K_a$ . The  $pK_a$  values of trichloroacetic acid and 1-naphthoic acid were obtained for the first time by the proposed method.

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