The Electrochemical Behavior of Methylene Blue at a Microcylinder Carbon Fiber Electrode

Huangxian Ju, Jun Zhou, Chenxin Cai,* and *Hongyuan Chen*

Department of Chemistry, Nanjing University, Nanjing 210093, P.R. China

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Abstract
The electrochemical behavior of methylene blue (MB) at a carbon fiber microcylinder electrode, was studied by cyclic voltammetry. The charge transfer coefficient α of the electrode reaction with two-electron transfer is 0.5, and the number of H^+ participating in the electrode process is 3 at pH 2.2–5.4, 2 at pH 5.4–6.0 and 1 at pH 6.0–10.7, respectively. The standard electron transfer rate constant $k^{o'}$, and standard formal potential $E^{o'}$ of MB at various pH were determined by using the carbon fiber microcylinder electrode. The electrode reaction mechanism of methylene blue at various pH is proposed. The adsorbability of MB at the electrode is discussed and explored by cyclic voltammetry and chronocoulometric technique.

Keywords: Microelectrode, Microcylinder carbon fiber electrode, Methylene blue, Electrode reaction kinetics

1. Introduction

Recently, the investigation of microelectrodes has been rapidly developed and become a larger research field [1, 2] because of their many advantages over normal electrodes in some applications such as voltammetry in fluid systems [3], capillary zone electrophoresis [4] and measurements in vivo [1] etc. However, the study of electrode reaction kinetics at a microelectrode, especially at a microcylinder electrode at its usual scan rate has been very rare, and to our knowledge, the study of the electrode reaction mechanism at a microelectrode has not been reported yet.

Now, the study of catalytic reactions at electrodes modified with mediators or promoters has attracted considerable attention [5, 6]. Bartlett et al. [7] reviewed the various ways that the surface of an electrode may be modified, or a mediator employed, to facilitate efficient electron transfer between the biomolecules and the electrode. Methylene blue (MB) is a dye that belongs to the thiazine family, it is a redox indicator with the formal potential in the range of –0.1 to –0.4 (vs. SCE) in pH 4–11 mediums, which is close to the redox potentials of many biomolecules, and thus, it had been used as an electron transfer mediator [8]. Although the electrochemical properties of MB at a normal bare, especially on mercury, or Nafion modified electrode have been extensively investigated with different electrochemical techniques [8–17], few kinetic parameters have been reported because the electrode process was considered as a reversible reaction at a normal electrode. The electrode reaction mechanism at various pH has not been explained systematically so that the mechanism is little understood [11, 13].

In this work, the electrochemical properties, the electrode reaction kinetics, and the electrode reaction mechanism were studied with a carbon fiber microcylinder electrode. The adsorbability of MB at the electrode was also discussed. These data provide important information for the fabrication of an MB modified microelectrode and furthermore, present a method mainly for the studies of electrode process and electrode reaction kinetics at a microcylinder electrode.

2. Theory

Because of the enhanced mass transport rate of a microelectrode, many reversible or quasireversible electrode processes at conventional electrodes are changed into quasi- or irreversible electrode processes at a microelectrode [1, 18]. For a quasi- or irreversible electrode process, the dependence of the peak potential of single sweep voltammetry on scan rate v as well as the charge transfer coefficient α at a microcylinder electrode is [19]:

$$E_{p,c} = \text{constant} - 0.5\,RT/(\alpha nF \ln v) \quad (1)$$

So the charge transfer coefficient α can be obtained from the slope of $E_{p,c} \sim \ln v$ curve in identical system.

The dependence of peak potential on standard electron transfer rate constant $k^{o'}$, α as will as v of anodic or cathodic electrode process at a microcylinder electrode is, respectively [20]

$$(1-\alpha)\zeta_{p,a} = \frac{1.8\,p(1-\alpha)^{\frac{1}{2}}\lg[p(1-\alpha)^{\frac{1}{2}}]}{1.4 + p(1-\alpha)^{\frac{1}{2}}} + 1.6 - 2.3\lg(k^{o'}r/D) \quad (2)$$

$$\alpha\zeta_{p,c} = -\frac{1.8\,p\alpha^{\frac{1}{2}}\lg(p\alpha^{\frac{1}{2}})}{1.4 + p\alpha^{\frac{1}{2}}} - 1.6 + 2.3\lg(k^{o'}r/D) \quad (3)$$

where $\zeta_p = (nF/RT)(E_p - E^{o'})$, $p = [(nFr^2v)/(RTD)]^{1/2}$, thus, the following formula can be obtained from Equations 2 and 3:

$$E^{o'} = E_{p,a} - \alpha(E_{p,a} - E_{p,c}) \quad (4)$$

The formal potential of depolarizer can be calculated with Equation 4, α, as well as $E_{p,a}$ and $E_{p,c}$ obtained from a cyclic voltammogram. When $\alpha = 0.5$, Equation 5 can be obtained from Equations 2 and 3.

$$\Delta\zeta_p = \frac{7.2p\lg(0.71p)}{2.0 + p} + 6.4 - 9.21\,g(k^{o'}r/D) \quad (5)$$

Thus, $k^{o'}$ at a microcylinder electrode can be determined with cyclic voltammetry and Equation 2 or 3 (when $\alpha = 0.5$, with Eq. 5).

3. Experimental

3.1. Instruments

Electrochemical measurements were carried out by using a

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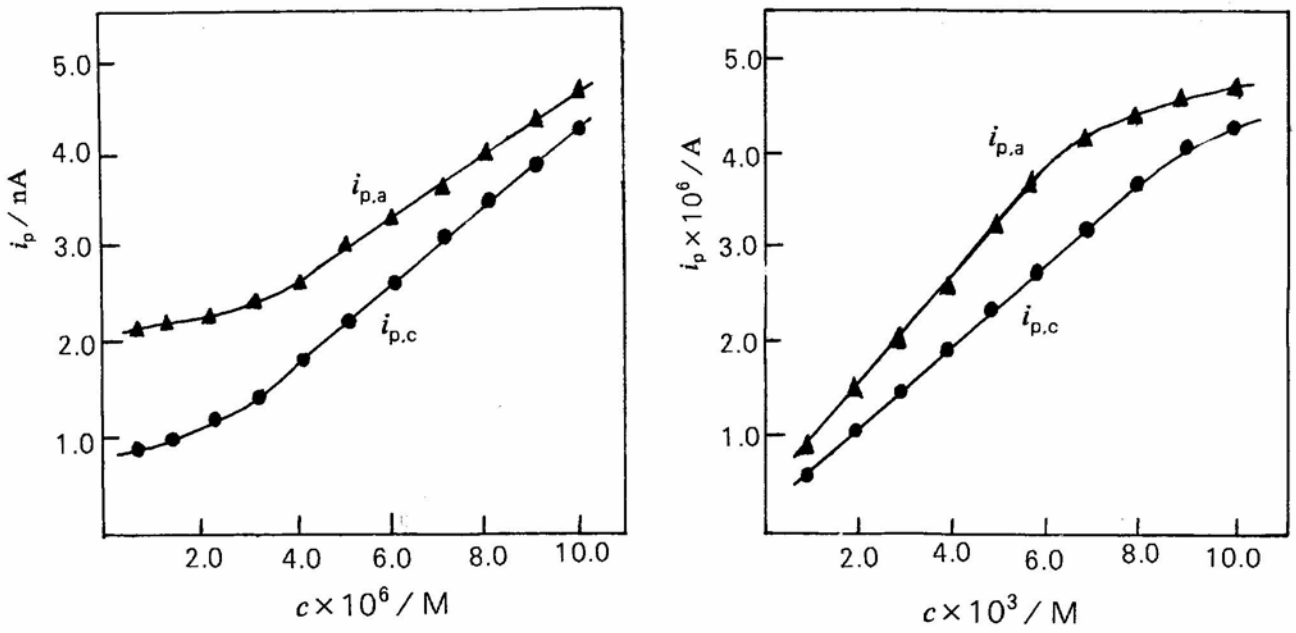

Fig. 1. Dependence of i_p on concentration of MB in pH 7.2 buffer solution at $v = 100$ mV/s.

BAS-100B Electrochemical Analyzer (BAS, USA) with a PA-1 Preamplifier (BAS, USA) which was used to amplify current and filter out noise. An FPG-310 Color Plotter (Fujitsu Company, Japan) was used to record voltammograms. The temperature was controlled at 20 ± 0.1°C with a thermostat.

3.2. Reagents

Methylene Blue with three waters of hydration ($C_{16}H_{18}N_3SCl \cdot 3H_2O$) and a purity of >99% was obtained from the Shanghai Third Chemical Reagent Factory in China, and was used as received without further purification. The reagents making up B-R buffer solution (pH 2–11, 0.040 M) were of analytical reagent grade. Double-quartz-distilled water by subboiling distiller was used throughout all experiments.

3.3. Procedure

The fabrication and pretreatment of carbon fiber microcylinder electrodes were similar to that previously reported [18, 21]. Briefly, single carbon fiber (PAN type) with 6–8 μm diameter (obtained from Shanghai Synthetic Fiber Research Institute) was sealed in capillary glass with Epon 812 epoxy resin (New York, USA). The carbon fiber microcylinder electrode with a length of ca. 2 mm was washed thoroughly with acetone and distilled water in an ultrasonic bath, and then was electrochemically pretreated in 1.0 M H_2SO_4 solution with trigular-wave potential sweep from −1.0 V to +2.0 V at the scan rate of 20 000 mV s for 5 min.

A three-electrode system with saturated calomel electrode (SCE) as reference, Pt wire as counter and pretreated carbon fiber microcylinder electrode as working electrode was employed. After deaerating with N_2 for 10 min, the electrochemical measurements were carried out under N_2 atmosphere.

4. Results and Discussion

4.1. The Dependence of Peak Current on Concentration of MB

The cyclic voltammetric responses of MB at various pretreated carbon fiber microcylinder electrodes are different. At an electrochemically unpretreated electrode, not only is the peak current very low and the difference of peak potentials large, but also the peak shape is very poor. However, at an electrochemically pretreated electrode, the peak shape is improved, and the response has approximately a 15-fold increase in sensitivity (over no pretreatment). The electrochemical treatment improves heterogeneous electron transfer rate for the redox couple at a carbon fiber microcylinder electrode. The results are similar to these mentioned in the literature [22, 23]. Thus, the following experiments were carried out at the electrochemically pretreated carbon fiber microcylinder electrode.

The dependence of peak current on concentration of MB is shown in Figure 1. When the concentration of MB is lower than 10^{-7} M, the peak current hardly changes. In the range of 4×10^{-6} to 6×10^{-3} M, both the oxidation and reduction peak currents increase linearly with increasing concentration of MB. When the concentration c of MB is larger than 6×10^{-3} M, the slope of i_p vs. c decreases with the increase of c (Fig. 1). The result is similar to that in the literature [11, 24–27], in which the phenomenon was explained by postulating the formation of dimers or higher aggregates in higher concentrations (above 10^{-2} M [26]). Spencer et al. [28] measured the equilibrium constant for dimerization as 3.97×10^3 M using temperature jump techniques.

4.2. The Effect of pH on Cyclic Voltammogram and Peak Potential

All the cyclic voltammograms, which were obtained after the microcylinder electrode was just placed in pH 2.2 to 10.7 buffer

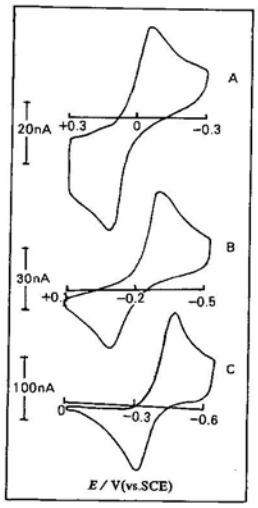

Fig. 2. Cyclic voltammograms of MB at microcylinder carbon fiber electrode in buffer solution including 1.0×10^{-4} M MB, $v = 100$ mV/s. A) pH 2.2, B) 5.8, C) 10.3.

solutions including 1.0×10^{-4} M MB, show a couple of redox peaks (Fig. 2). With increasing pH, the peak potentials of both oxidation and reduction peaks shift in a negative direction with two changes in slope at pH 5.4 and pH 6.0 (Fig. 3). $\partial E_{p/2,c}/\partial$pH is −87 mV/pH at pH < 5.4, −58 mV/pH at pH 5.4–pH 6.0 and −28 mV/pH at pH > 6.0. The number of electrons transferred in the electrode reaction process for MB is 2 [11], thus, the number of H^+ participating in the electrode process is 3 at pH < 5.4, 2 at pH 5.4–6.0 and 1 at pH > 6.0. The results are close to these at normal macroelectrodes [12, 17, 25], but in these three references, the experiments in pH 5.4 to 6.0 solutions had not been carried out, thus the particular results at pH 5.4–6.0 had not been reported. Therefore, it was inadequate that two H^+ were given in the electrode reaction equation of MB [12, 13].

The difference of the peak potentials in a cyclic voltammogram is less at higher pH (Fig. 2C) or lower pH (Fig. 2A), however, the difference is larger at pH 5.8 (Fig. 2B). The peak current increases with increasing pH. All of these changes result from the concentration cf H^+, the surface state of carbon fiber electrode, and various electrode reaction mechanisms in various ranges of pH.

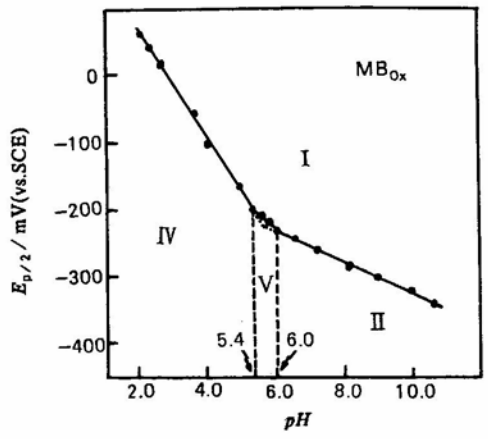

Fig. 3. Dependence of $E_{p/2,c}$ on pH, experimental conditions are the same as Figure 2.

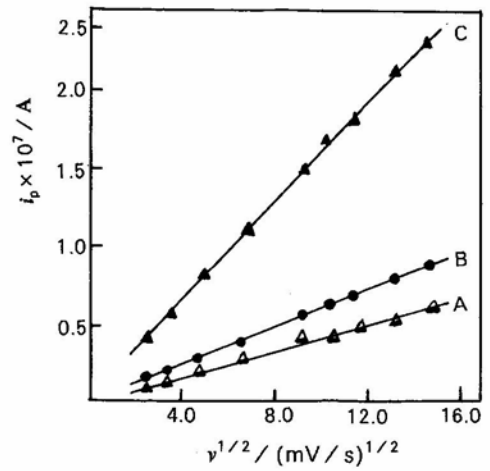

Fig. 4. Plots of $i_{p,c}$ vs. $v^{1/2}$, experimental conditions are the same as Figure 2.

4.3. The Effects of Scan Rate on Peak Current and Peak Potential

Figure 4 shows that the peak currents of MB in various pH solutions (which were obtained in a 1×10^{-4} M MB solution) are proportional to $v^{1/2}$. The peak potential also shifts with the increasing scan rate (Fig. 5), thus, the electrode reaction is not a reversible or surface controlled process. The slope of $i_{p,c}$–$v^{1/2}$ curve increases with the increasing pH, indicating that the electrode reaction rate is also increased. On the electrochemically pretreated carbon fiber electrode surface, there is a great quantity of the functional group of –COOH [21–23]. The concentration of $-COO^-$ group, which is formed from the ionization of –COOH on the electrode surface, increases with the increasing of the pH. It not only increases the concentration of MB with a positive charge on the electrode surface, but also is advantageous to the discharge MB at the electrode. Thus, the electrode reaction rate is larger at a higher pH.

As the logarithmic value of scan rate increases, the oxidation peak potential shifts linearly in a positive direction, and the reduction peak potential also shifts linearly in a negative direction. At various pH, the shifts of both anodic and cathodic peak potentials are of the same slope (e.g., Fig. 5 for $E_{p,c}$). Thus, the charge transfer coefficient $\alpha = 0.50$ was obtained from the slope and Equation 1.

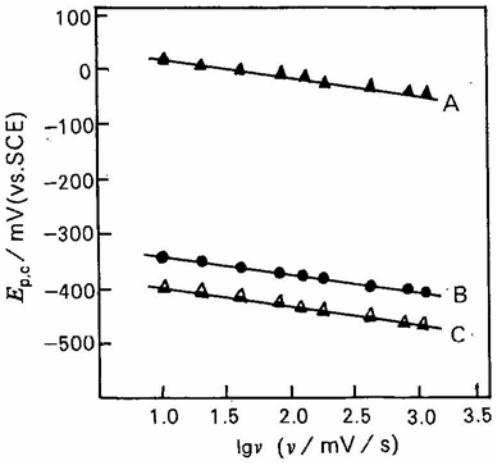

Fig. 5. Curves of $E_{p,c}$ vs. lg v, experimental conditions are the same as Figure 2.

Table 1. Standard electron transfer rate constants $k^{o'}$ and standard formal potentials $E^{o'}$ for MB at microcylinder carbon fiber electrode (v = 100 mV/s).

pH	2.30	4.00	4.50	4.90	5.80	6.68	8.30	8.80	9.59	10.30
ΔE_p [mV]	180	220	200	180	230	190	170	150	140	140
$E^{o'}$ [mV]	+40	−85	−130	−170	−185	−295	−305	−315	−345	−370
$k^{o'} \times 10^3$ [cm/s]	2.54	1.12	1.72	2.54	0.96	2.09	3.08	4.54	5.52	5.52

4.4. The Determination of Standard Electron Transfer Rate Constant $k^{o'}$

From Equation 4 and α value of 0.5, the equation of $E^{o'} = (E_{p,a} + E_{p,c})/2$ can be obtained. The results of $E^{o'}$, ΔE_p and $k^{o'}$ calculated with Equation 5 at various pH are shown in Table 1 ($n = 2$, $D = 7.6 \times 10^{-6}$ cm^2/s [11], and the radius of electrode (Table 1) $r = 3.8 \times 10^{-4}$ cm). The values of $E^{o'}$ at various pH are close to these in the literature, in which $E^{o'}$ is +0.10, −0.02, −0.19, −0.26 and −0.34 V at pH 2.0 [17], 2.9 [9], 4.9, 6.7 and 9.2 [10], respectively. Other data have not been reported yet.

The results indicate that the effects of pH on ΔE_p, $E^{o'}$ and $k^{o'}$ are very complicated. The whole electrode process is affected by two opposing actions. At lower pH, the reduction reaction with the participation of H^+ is quickened, however, it is disadvantageous to the ionization of the group –COOH on the carbon fiber surface to form $-COO^-$ which can increase the concentration of MB with a positive charge on the electrode surface. At higher pH, it is disadvantageous to the electrode reaction with the participation of H^+, but MB approaches the electrode surface more easily with the group of $-COO^-$, which is advantageous to the discharge of MB at the electrode. As a result of these two opposite effects, two maximum values of ΔE_p (the least of $k^{o'}$) occur between pH 2.3 to 10.3, and the fluctuations of ΔE_p and $k^{o'}$ only occur in the range of pH < 6.0 with the participation of more H^+. When pH > 6.68, only one H^+ participates in the electrode reaction, the effect of electrode surface group on reaction rate is larger than the effect of protonation, thus $k^{o'}$ increases with the increasing of the pH.

4.5. The Electrode Reaction Mechanism

The electrochemical behavior of MB at the microelectrode is different at various pH because the number of H^+ participating in the electrode process is related to the pH of the solution. Though the number of H^+ participating in the electrode process at various pH had been obtained [11, 17, 25], the reaction mechanism taking the acid-base properties of the leuco methylene blue at various pH into account has not been reported yet. Electrode reactions with one electron transfer were given in the outline of the mechanism with 2 H^+ in acid and 1 H^+ in neutral medium in the literature [13]. Here three references ([40, 41, 43]) were cited to verify the scheme, but reference [41] reported that the number of electron transfer is 2, and reference [40] did not give the numbers of electron transfer and H^+ participating reaction.

Because MB has the same constitution as the other five dyes reported in the literature [6], the scheme of the electrode reaction of MB at a microcylinder carbon fiber electrode can be shown in Figure 6 from the above results. When pH < 5.4, first of all quinonoid MB (I) combines with 1 H^+ to form III and then III obtains two electrons and 2 H^+ to form hydroquinonoid IV, or quinonoid I combines directly with two electrons and 3 H^+ to form IV. When 5.4 < pH < 6.0, MB (I) obtains two electrons and 2 H^+ to form V; and then pH > 6.0, MB (I) obtains two electrons and 1 H^+ to form II directly. In fact, for the leuco methylene blue, II is a base, IV is a binary acid, and V is a mediator in the acid-base balance between II and IV. The acid dissociation constants are $10^{-5.4}$ (0.40×10^{-5}) and 1.00×10^{-6}, respectively. The results are consistent with the literature [29] in

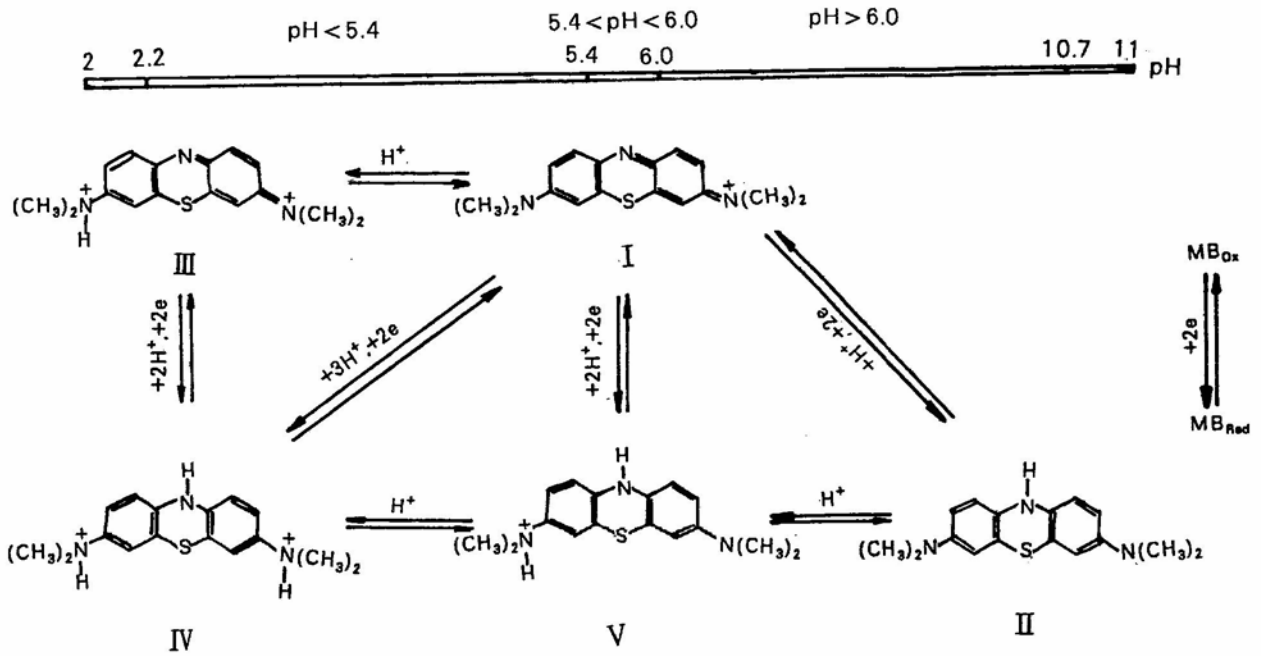

Fig. 6. Electrode reaction mechanism for MB at a microcylinder carbon fiber electrode at various pH.

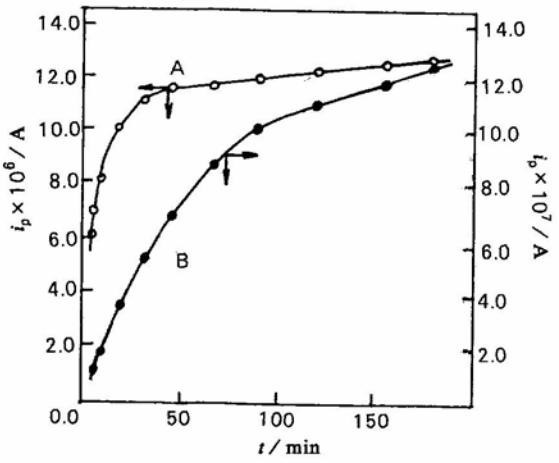

Fig. 7. Relation of peak current and immersion time, A) for 1.0×10^{-3} and B) for 1.0×10^{-5} M MB in pH 7.2 buffer solution, $v = 100$ mV/s.

which Clark et al. presented the reduced form, leuco-methylene blue, as a binary acid with the acid dissociation constants of 0.95×10^{-5} (K_1) and 1.36×10^{-6} (K_3) at 20 °C.

4.6. The Adsorbability of MB at the Microcylinder Carbon Fiber Electrode

After a microcylinder carbon fiber electrode has been dipped in 1×10^{-4} M MB solution (pH 7.2) for 1 h, the peak current is proportional to v. Thus, the electrode process is controlled by the adsorption of MB. Because the adsorption of the depolarizer has a marked effect on the capacity of the double-layer, in comparison with the base line of a.c. voltammograms in the absence and in the presence of MB, the evidence indicates that both reactant MB and its reduced product adsorb on the electrode surface.

4.6.1. Dependence of Adsorbance on Immersion Time

The reduction peak current of MB increases with the increasing of time that the electrode is immersed in a pH 7.2 buffer solution including MB, and tends to a steady value (Fig. 7). Thus, the adsorbance also increases with increasing adsorptive time, and the adsorption of MB on the electrode surface reaches equilibrium after a longer time. Furthermore, the time to reach adsorptive equilibrium is longer at a lower concentration of MB.

4.6.2. The Effect of pH on Adsorbability

Both the time to rach adsorption equilibrium and adsorbance are relative to this pH of the solution. At higher pH, the time to reach saturated adsorption is shorter in the solution with the same concentration of MB.

The adsorbance also increases with raising of the pH due to the increase of $-COO^-$ group formed from the ionization of $-COOH$ on the electrode surface. Furthermore, the stability of adsorbed MB at a higher pH is better.

4.6.3. The Determination of Adsorbance

After the electrode was dipped in 1.0×10^{-3} M MB solution (pH 7.2) for 1 h, a chronocoulometric experiment was carried out in a buffer solution without MB. The adsorbance of MB at the electrode can be obtained from the following Equation:

$$Q = nFA\Gamma \tag{6}$$

Where Q is the charge quantity consumed coulometrically in a complete reduction of MB, Γ is the adsorbance of per unit area and other symbols have their usual meaning. The geometric area of the microcylinder electrode A is 4.6×10^{-4} cm^2. $\Gamma_{exp} = 1.4 \times 10^{-9}$ mol/cm^2 was obtained from the chronocoulometric experiment for saturated adsorption. The horizontal section area of the MB molecule S is 0.75 nm^2 [30], thus, the theoretical monolayer adsorbance of MB at the electrode Γ_{theory} is 2.2×10^{-10} mol/cm^2, and $\Gamma_{exp}/\Gamma_{theory} = \eta = 6.4$. At a carbon electrode, the experimental absorbance is generally 5 times larger than the theoretical value due to the rough electrode surface [31]. η is just close to the value, thus, the adsorption of MB at carbon fiber microcylinder electrode is monolayer in character.

4.6.4. The Stability of MB Adsorbed on the Electrode

The voltammograms obtained in a pH 7.2 solution using the scan rate of 100 mV/s from 0.10 V to −0.60 V at the electrode which was prepared by dipping a electrochemically pretreated carbon fiber into pH 7.2 buffer solution containing 1.0×10^{-3} M MV for 1 h, indicated that a pair of peak currents decreased considerably with repetitive sweeps. The cathodic peak current declines following the first kinetic expression. The half-life is 87 s. Thus, the stability of MB modified carbon fiber microcylinder electrode fabricated with adsorptive method is worse than that at a normal glassy carbon electrode in the literature [8]. The fabrication of an MB modified microelectrode with a polymeric method will be reported in another article.

5. Acknowledgement

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6. References

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