Effect of Halide Ions on the Adsorption Prewave of Methylene Blue

By

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Synopsis

In the present study, the familiar Langmuir adsorption isotherm is applied to the mixed adsorption of methylene blue in the presence of halide ion. The variation of methylene blue prewave height or AC peak height with halide ion concentration is treated statistically. It is concluded that the decrease in the DC prewave or in the corresponding AC peak height is caused by the mixed adsorption of halide ion. The relative temperature coefficient of AC peak height was found to be 1.04% deg⁻¹ at 25°C in 0.4M KNO₃ with acetate buffer solution (pH 4.7).

Introduction

The electrode process of methylene blue on a dropping mercury electrode was first clarified by Brdicka¹⁾. It was concluded that the process is the reduction-oxidation reaction with adsorption phenomenon. Electroactive substances, such as the leucoform of methylene blue and diethyldithiocarbamate, give a high sensitivity in electroanalytical determination, especially, in AC or high-frequency polarography²⁻⁴⁾. The adsorption prewave and also the corresponding AC peak height of methylene blue is affected by chloride and bromide ions⁵⁾; iodide ion reduces methylene blue to the colorless leucoform.

Theory of Mixed Adsorption of Methylene Blue and Halide Ion.

If the halide ion, X^- , is mixed-adsorbable with methylene blue on the mercury electrode surface, Langmuir adsorption isotherm might be applied as follows.

$$a_{MB} = \frac{Z\omega_{MB}[MB]}{1 + \omega_{MB}[MB] + \omega_X[X^-]} \quad (1)$$

In this equation, a_{MB} is the number of moles of methylene blue leucoform adsorbed on 1 cm² of the electrode surface, Z represents the maximum number of moles adsorbable per unit area of surface, ω is the adsorption coefficient, $[]$ is the equilibrium concentration at the electrode surface, and the suffices MB and X^- refer to methylene blue and halide ion, respectively.

If the adsorption equilibrium is attained quickly, as soon as the new drop surface is formed, and if a_{MB} is directly proportional to the DC polarographic prewave height, as first proposed by Brdicka, and further to the AC peak height of methylene blue, it may be expected that between the halide ion concentration and the reciprocal of i_{DC} a linear relationship should hold; i.e.

$$\frac{1}{i_{DC}} = \frac{a[X^-]}{C_{MB}} + b \quad (2)$$

Analogously, one has for the AC peak height i_{AC}

$$\frac{1}{i_{AC}} = \frac{a' [X^-]}{C_{MB}} + b' \quad (3)$$

where a , b , a' and b' are constants.

Experimental

Apparatus A Yanagimoto polarograph, type PA-102, was used. In AC polarographic measurement, the cell was a modified Kalousek cell with a separated saturated calomel electrode as the reference, which was connected to the electrolysis cell by an agar bridge with saturated KNO_3 . The cell was short-circuited between mercury pool and the SCE by a 1000- μF condenser. The electrolysis solutions were degassed with pre-purified nitrogen gas during the measurement. The temperature of the cell, except in the study of temperature dependence, was thermostatted to $25 \pm 0.1^\circ\text{C}$. The pH value of the solution was measured with a glass electrode pH meter (Hitachi-Horiba, model F-5). The dropping mercury electrode used had the mercury flow rate of 1.15 mg sec^{-1} and the drop time of 6.48 sec at the mercury pressure, $h=80$ cm. These values were measured in an air-free water at the open-circuit.

Reagents $10^{-3} M$ methylene blue standard solution was prepared from a Merck AG product for microscopy. According to Wopschall and Shain⁹, the methylene blue specimen was considered to contain two hydration waters. All the other chemicals used were of an analytical reagent grade. Water used was first put through a deionizer, and then distilled. Maximum suppressor was not employed. Buffer solutions were prepared according to the Walpole's system, $0.2 M \text{CH}_3\text{COOH}$ - $0.2 M \text{CH}_3\text{COONa}$. The electrolysis solution usually contained 10 ml of the above buffer solution in the total volume of 25 ml.

Results and Discussion

DC and AC polarograms of methylene blue and regression analysis.

In the DC polarography, only a single reduction prewave is observed with the concentration lower than the critical concentration of $5 \times 10^{-5} M$ ⁵, and the main wave does not appear. Figures 1 and 2 illustrate the DC and AC polarograms with the supporting electrolyte, that is, $0.4 M$ in potassium nitrate containing acetate buffer (pH 4.7), to which various amounts of potassium bromide are added. Further, it was found that methylene blue peak is also slightly suppressed by the addition of chloride ion. The chloride ion in concentrations higher than $1 \times 10^{-2} M$ interferes with methylene blue peak remarkably. The AC polarographic peak is distinctly prominent as is shown in Fig. 2. With the increasing halide ion concentration, however, the half-wave potential of anodic halide wave is shifted to the more positive potential and finally overlaps the methylene blue wave.

The regression analysis is applied to the equations, (2) and (3), and the regression coefficient, r , is evaluated. The result is summarized in Tables I-III, and shown in Figs. 3-5.

According to equation (3), the slope of straight line in Fig. 5 should be inversely proportional to the methylene blue concentration. The slope values estimated statistically are given in Table III and the slope ratio is shown in Table IV. A fairly good

Fig. 1. DC polarographic adsorption prewave of $5 \times 10^{-5} M$ methylene blue in $0.4 M KNO_3 + \text{acetate buffer (pH 4.7)}$ containing KBr. The KBr concentration is (a) $1 \times 10^{-5} M$, (b) $5 \times 10^{-5} M$, (c) $1 \times 10^{-4} M$, (d) $1 \times 10^{-3} M$.

Fig. 2. AC polarographic wave of methylene blue corresponding to Fig. 1.

Fig. 3. The relationship between the reciprocal of the DC wave height and the concentration of bromide ion added. The supporting electrolyte is the same as in Fig. 1.

Fig. 4. The relationship between the reciprocal of the AC peak height and the concentration of chloride ion added. The supporting electrolyte is $0.4 M KNO_3$ + acetate buffer (pH 4.7).

Fig. 5. The relationship between the reciprocal of the AC peak height and the concentration of bromide ion added. The supporting electrolyte is the same as in Fig. 1.

Table I. Regression analysis for the reciprocal of methylene blue wave height ($Y=1/i_{DC}$) and the bromide concentration ($X=[Br^-]$). (cf. Fig. 3)

MB concn.	Regression line	Result of t -test
$5 \times 10^{-5} M$	$Y = (5.66 \pm 0.500) \times 10^3 X + (5.34 \pm 0.022)$	$r_0 = 0.876 > r(19-2, 0.01) = 0.575$ $t_0 = 7.493 > t(17, 0.01) = 2.90$

Table II. Regression analysis for the reciprocal of methylene blue peak height ($Y=1/i_{AC}$) and the chloride concentration ($X=[Cl^-]$). (cf. Fig. 4).

MB concn.	Regression line	Result of t -test
$2 \times 10^{-5} M$	$Y = (13.73 \pm 0.77) \times X + (2.59 \pm 0.04)$	$r_0 = 0.973 > r(15-2, 0.01) = 0.641$ $t_0 = 15.25 > t(13, 0.01) = 3.01$

Table III. Regression analysis for the reciprocal of methylene blue peak height ($Y=1/i_{AC}$) and the bromide concentration ($X=[Br^-]$). (cf. Fig. 5).

MB concn.	Regression line	Result of t -test
$1 \times 10^{-5} M$	$Y = (1.08 \pm 0.05) \times 10^4 X + (5.14 \pm 0.14)$	$r_0 = 0.985 > r(12-2, 0.01) = 0.708$ $t_0 = 3.195 > t(10, 0.01) = 3.169$
$2 \times 10^{-5} M$	$Y = (4.85 \pm 0.467) \times 10^3 X + (2.59 \pm 0.016)$	$r_0 = 0.984 > r(15-2, 0.01) = 0.641$ $t_0 = 20.8 > t(13, 0.01) = 3.01$
$3 \times 10^{-5} M$	$Y = (2.28 \pm 0.065) \times 10^3 X + (1.66 \pm 0.032)$	$r_0 = 0.972 > r(25, 0.01) = 0.487 > r(26, 0.01)$ $t_0 = 20.91 > t(24, 0.01) = 2.80$

Table IV. The slope ratio of the regression lines shown in Fig. 5.

Concentration of MB, M	Slope of regression line	Relative ratio of slope (found)	Reciprocal of the MB concn. ratio (theoretical slope ratio), $\times 10^5$
1×10^{-5}	1.08×10^4	1.00	1.00
2×10^{-5}	4.85×10^3	0.451	0.50
3×10^{-5}	2.28×10^3	0.212	0.33

The denominator is the slope of $1 \times 10^{-5} M$ methylene blue, and the numerators, the slopes of $3 \times 10^{-5} M$, $2 \times 10^{-5} M$ and $1 \times 10^{-5} M$, respectively.

accordance is found.

Electrocapillary curve

As is well known, the electrocapillary curve can offer some important information as to adsorption phenomena. Figure 6 shows the relationship between the drop time and the potential of dropping mercury electrode. Methylene blue clearly lowers the interfacial tension as the result of adsorption of the reduced form at the mercury surface. Furthermore, with increasing bromide ion concentration, the interfacial tension is lowered at the potential of methylene blue prewave. Namely, the bromide ion is evidently adsorbed onto the dropping mercury electrode with methylene blue. Such a phenomenon is also observable in the electrocapillary curve of methylene blue solution to which chloride ion is added. This fact indicates most strongly the evidence for the mixed adsorption of methylene blue and halide ion.

Fig. 6. The electrocapillary curves of $5 \times 10^{-5} M$ methylene blue in the supporting electrolyte as stated in Fig. 1.

The full line : without KBr ; $\circ$: $1 \times 10^{-3} M$ KBr ; $\bullet$: $1 \times 10^{-4} M$ KBr ; $\triangle$: $1 \times 10^{-5} M$ KBr.

The temperature dependence of AC polarographic peak height of methylene blue in various electrolyte solutions

According to several authors^{1, 7, 8)}, adsorption current shows various temperature dependences, for example, as summarized by Zuman⁹⁾. With several kinds of supporting electrolyte, the temperature dependences of AC peak height are measured, as summarized in Table V.

Table V. The relative temperature coefficient of $2 \times 10^{-5} M$ methylene blue AC peak height at $25^\circ C$ in various supporting electrolyte solutions.

Supporting electrolyte	Temperature range, $^\circ C$	Relative temperature coefficient
$0.4 M NH_4OH-0.4 M NH_4NO_3$	2-45	$1.61\% \text{ deg}^{-1}$
$*0.08 M Na_2C_2O_4-0.16 M H_2C_2O_4$	5-15	$0 \text{ } \%$
	15-52	$-1.10\% \text{ deg}^{-1}$
$0.4 M H_2SO_4$	1-50	$-1.35\% \text{ deg}^{-1}$
$0.4 M KNO_3 + \text{Acetate buffer (pH 4.7)}$	2-50	$1.04\% \text{ deg}^{-1}$

Measurements were carried out versus mercury pool.

The sufficient conductivity of the electrolysis solution was confirmed by the variation of electrode distance.

* If the temperature becomes below $5^\circ C$, precipitation occurs.

Summary

The mixed adsorption of methylene blue and halide ion was investigated. On the basis of Langmuir adsorption isotherm, it was predicted that a linear relationship exists between the reciprocal of the DC wave height, or of the AC peak height, and the halide ion concentration. Experimental results showed the essential validity of the theoretical prediction. Finally, the temperature dependences of methylene blue peak height had been studied by the AC polarography.

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メチレンブルーの吸着前置波におよぼすハロゲン化物イオンの影響

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ハロゲン化物イオンの存在のもとでメチレンブルーの混合吸着にラングミュア吸着等温式を適用した。メチレンブルー吸着前置波高、あるいは交流ピーク波高とハロゲン化物イオン濃度との間の変動を統計学的に取扱った。直流前置波高の減少、あるいは対応する交流ピーク波高のそれは、ハロゲン化物イオンの混合

吸着によって引き起こされると結論される。また、このことは電気毛管曲線の結果から明らかである。さらに、メチレンブルーの交流ピークの温度依存性が、種々の支持電解質中で検討され、酢酸緩衝溶液を含む0.4M 硝酸カリウム中では、25°Cにおける相対温度係数は $1.04\% \text{ deg}^{-1}$ であった。