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Zhaoxi Liang^a; Xiaoyun Wang^a; Yi He^a

^a Institute of Polymer Science, Zhongshan University, Guangzhou, China

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ELECTROREDUCTION KINETICS OF ALKYL POLYVIOLOGENS STUDIED BY *IN SITU* SPECTROSCOPY

Zhaoxi Liang, Xiaoyun Wang and Yi He
(*Institute of Polymer Science, Zhongshan University,
Guangzhou, China, 510275*)

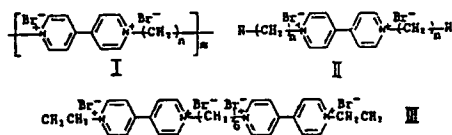
Abstract

The electroreduction kinetics of several alkyl polyviologens (I), such as polypropyl viologen, polybutyl viologen, polyhexyl viologen as well as their respective low molecular analogs (II) and a bisviologen have been studied by *in-situ* spectroscopy. The reaction order (α) and rate constant (k) of the 1st electroreduction have been calculated according to $dA/dt = kC^\alpha$. The results show that the effect of alkyl chain length (n) is obvious for II, k values decrease in the order: PrV > BV > HxV. k values of I are lower than those of II and depend on M_w , but slightly on n . These facts may be attributed to the diffusion-controlled nature of the electroreduction process. The influences of viologen concentration, the supporting electrolyte and the pH value have also been investigated. In general, the memory time of I is longer than those of II.

INTRODUCTION

The viologen, a kind of redox compound, can undergo two-step reduction accompanied by obvious color changes induced by electric current. It has a number of important advantages over the inorganic materials^[1], such as relatively high charge efficiency, quick response time, ease in molecular design. Therefore it has been of great interest in electrochromic display application.

The electroreduction of viologen in solution has been extensively studied^[2-4], but comparatively little is known about the electroreduction kinetics. In order to study the electroreduction kinetics of alkyl polyviologens and their



low molecular analogs, some polyviologens with main chain structure as I ($n=3, 4, 6$ abbreviated PPrV, PBV, PHxV respectively) and alkyl viologen II ($n=3, 4, 6$ abbreviated PrV, BV, HxV respectively) and bisviologen III (EtV-Hx-EtV) have been synthesized and the electroreduction kinetics has been studied by *in-situ* spectroscopy.

EXPERIMENTAL

Materials

Alkyl viologens, polyviologens and bisviologen were synthesized as described in our previous paper⁽⁵⁾. The molecular weight (M_w) of polyviologen was determined by the laser scattering method.

Electroreduction Kinetics

Kinetics study was carried out in a quartz cell (Fig. 1), an ITO glass electrode was placed in the sample beam position of a Shimadzu UV-240, then monitored the *in-situ* changes of the absorption maximum of V^+ with time during electroreduction. According to the equation $dA'/dt = kC^\alpha$, the reaction order (α) and the rate constant (k) of 1st electroreduction can be calculated.

Memory Time (MT)

MT, defined as the recovery time of V^+ to V^{2+} simultaneously after the applied voltage being cut off, was measured by using the same apparatus as described in Fig. 1.

RESULTS AND DISCUSSION

Influence of Viologen Structure

The results listed in Tab. I show that the effect of alkyl chain length (n) is obvious for II, k values decrease in the order: PrV > BV > HxV, in the case of I, k values are lower than their low molecular analogs (Fig. 2) and depend on M_w , but slightly on n . According to our previous work⁽⁶⁾ the electrode process of first electroreduction is diffusion-controlled, consistent with the Nernst equation, therefore k values of the viologens with longer alkyl chain may be lower as well as the polyviologens with higher M_w due to their slower diffusion rates.

Dependence of Electroreduction Rate upon Viologen Concentration (C)

In Fig. 3, it is clear that the higher C of alkyl viologen, the faster is the electroreduction rate. However, for polyviologen, the rates increase with increasing C in the initial period (Fig. 4a, b) and later fall slightly with C (Fig. 4c). These facts may be interpreted as that the viologens absorbed on the electrode are being reduced at first and then the electrode process is diffusion-controlled, while at higher C , the entanglement of polyviologen themselves makes their diffusion more difficult, thus the rates fall slightly with increasing C .

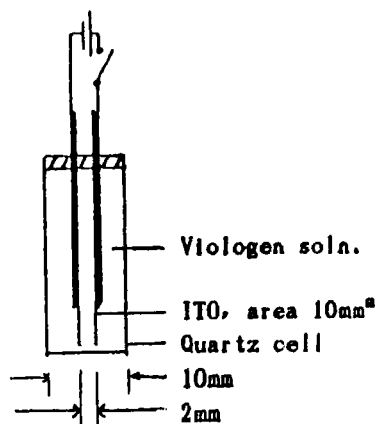


Fig. 1 ITO quartz cell for electroreduction

Tab. 1 k , α and MT values of viologens

Viologens	λ_{max} (nm)	k (L/mol.s)	α	MT (s)	M_w
PrV	550	357	1.49	72	400
BV	544	97.3	1.26	84	428
HxV	543	78.3	0.86	66	484
EV-Hx-EV	570	12.4	0.86	114	882
PPrV	536	10.4	0.85	138	4390
PPrV	536	8.64	0.74	--	7590
PBV	568	8.60	0.84	288	5470
PHxV	580	9.38	0.80	270	5600

[KBr]=0.3mol/L, pH=8.8, Input volt=0.7v

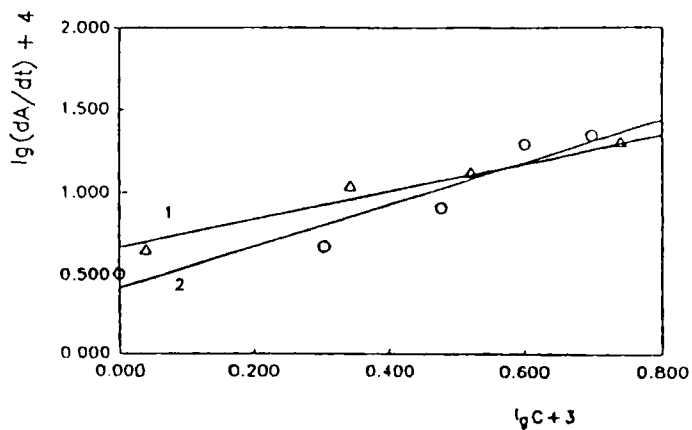


Fig. 2. Plots of $\lg \frac{dA}{dt} \sim \lg C$ for BV and PBV.

curve:	1	2
viologen:	BV	PBV
λ (nm):	656	668

[KBr]=0.3mol/l; pH=6.8; input volt.: 0.7 V.

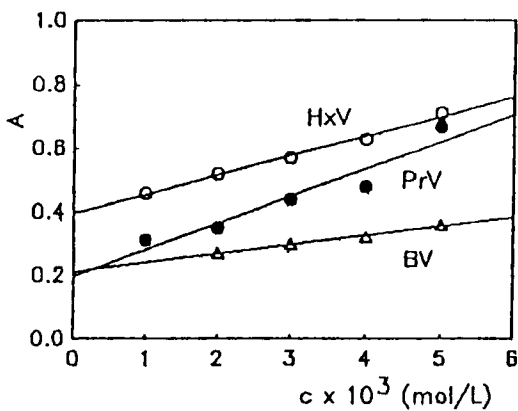


Fig. 3 Plots of A vs. conc. of viologens on 80 seconds

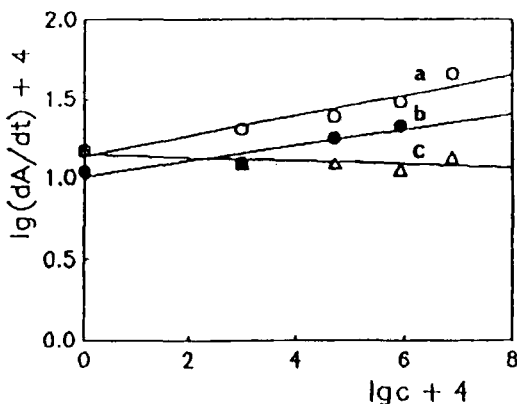


Fig. 4 Plots of $\lg(dA/dt)$ vs. $\lg C^T$ for PIIxV on various time

Curve:	a	b	c
$[\eta]$ (dl/g):	0.32	0.19	0.32
Time (min.):	0~1.0	0~3.0	1.0~3.0

Effect of Supporting Electrolyte

Tab. 2 shows the electroreduction rates decrease with the rising of [KBr]. The diffusion process can be considered as a self-diffusion process when [KBr] is much higher than C , it is understandable that the electroreduction rates decrease because the diffusion coefficients of viologens decrease with the increasing [KBr] according Onsager limiting equation^[7].

Either KCl or KBr used as supporting electrolyte, the rate is almost the same. However the rate decreases and precipitation takes place while KI is used as electrolyte.

Effect of pH

The electroreduction rates drop off with the raise of pH (Tab.3). Apparently, the rate can be strongly influenced by the state of the electrode surface, referable to the absorption and desorption of viologen. The ITO electrode surface is viewed to consist of hydroxyl groups which can be exchanged with a counter ion $X^{-[8]}$. At higher pH, it is unfavorable for the exchange equilibrium, thus presents the deposition of V^+ on the electrode surface. As regarding the stability of viologen, it is better to carry out the reduction in neutral solution.

Tab. 2 Effect of [KBr] on the electroreduction rate of viologens

[KBr] (mol/L)	dA/dt (mol/L.s)	
	PrV	PPrV
0.16	1.28	0.140
0.30	0.64	0.086
0.80	0.25	0.053

$$[V^{2+}] = 1.0 \times 10^{-3} \text{ mol/L}$$

Tab. 3 Effects of pH on k and α values for viologens

Viologens	pH=2.0		pH=6.8		pH=10.0	
	k (mol/L.s)	α	k (mol/L.s)	α	k (mol/L.s)	α
HxV	78.6	1.41	76.8	0.86	13.8	0.75
EV-Hx-EV	18.5	0.96	12.4	0.86	0.96	0.32
PHxV	3.7	0.59	9.36	0.80	0.84	0.30

Memory Time (MT)

The inherent memory, afforded by the reduced radical cations in the absence of O_2 , is an advantageous feature of these electrochromic display materials, that means to maintain the coloration on the electrode without any power consumption. In general, MTs of polyviologens are longer than those of their low molecular analogs that may be attributed to the diffusion-controlled nature of the electroredox process.

Acknowledgment

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