

Method of obtaining the thermodynamic characteristics of redox behaviour of vat dyes in aqueous media

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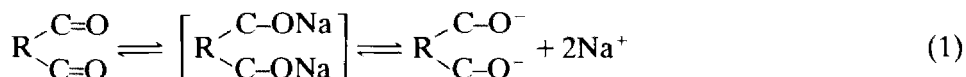
(Received 31 March 1993; accepted 10 May 1993)

Abstract

Cyclic voltammetry is suggested as a method for determining the thermodynamic characteristics of redox behaviour of vat dyes. In contrast to the existing methods of studying the redox properties of this class of dyes (spectrophotometric and potentiometric titration), the application of which is limited due to insolubility of the vat dyes, the suggested technique allows the investigation to be performed in an aqueous medium for the entire pH interval.

INTRODUCTION

Vat dyes are one of the most important classes of dyes for the colouration of textile materials of cellulose fibres, and recently also for those of blends of cellulose and synthetic fibres. These dyes are polycyclic aromatic compounds containing two or more quinone groups and they are insoluble in water. Application of vat dyes is characterized by their reduction in alkaline medium to change them into the soluble form (leuco compounds); under the conditions of the alkaline medium the leuco compounds exist completely in the form of the strongly ionized sodium salt [1] (see eqn. (1)).



In practice, the reduction of the vat dyes is a complicated heterogeneous reversible process consisting of a series of consecutive stages: chemical reactions, processes of dissolution and diffusion [2, 3]. Redox properties of

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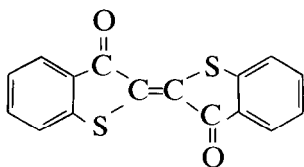


Fig. 1. Structural formula of thioindigo red C $\left(\begin{array}{c} \text{C=O} \\ \text{R} \\ \text{C=O} \end{array} \right)$.

the vat dyes can be estimated most precisely from their thermodynamic characteristics, but unfortunately thermodynamic data are practically absent from the literature. Hence the present paper is aimed at developing the technique of the estimation of thermodynamic characteristics of the redox behaviour of vat dyes in aqueous media using the method of cyclic voltammetry.

EXPERIMENTAL

Thioindigo red C, the structural formula of which is shown in Fig. 1, was the object of this investigation. The dye was purified according to the technique known and described earlier [4] by revatting followed by thorough washing. The purity of the dye obtained was controlled by the highly effective method of liquid chromatography.

The electrochemical measurements were conducted on a potentiostatic plant consisting of potentiostat, generator of signals of constant form, double-coordinate recorder and standard three-electrode electrochemical cell. The carbon-graphite working electrode was prepared according to the technique proposed elsewhere [5]. For this purpose, the side surface of the carbon-graphite rod was isolated by paraffin. The butt-end of the electrode contained the reactive mass consisting of technical elementary carbon, an aqueous emulsion of fluoroplaste and the substance investigated. A saturated silver-chloride electrode was used as a reference electrode. Platinum wire was used as an auxiliary electrode. All the measurements were conducted at 298 K in citrate-phosphatic buffer solutions that were deaerated with argon. The compensation for IR-decrease in tension was carried out according to the technique described in the manual for the potentiostat used. The potentials in the present paper are given relative to the hydrogen electrode.

RESULTS AND DISCUSSION

Because the process of the reduction of the vat dyes is determined by the presence of the quinone groups, it can be shown as the dependence on pH of the reaction medium as the formation of hydroquinone or hydroquinone

ion proceeds

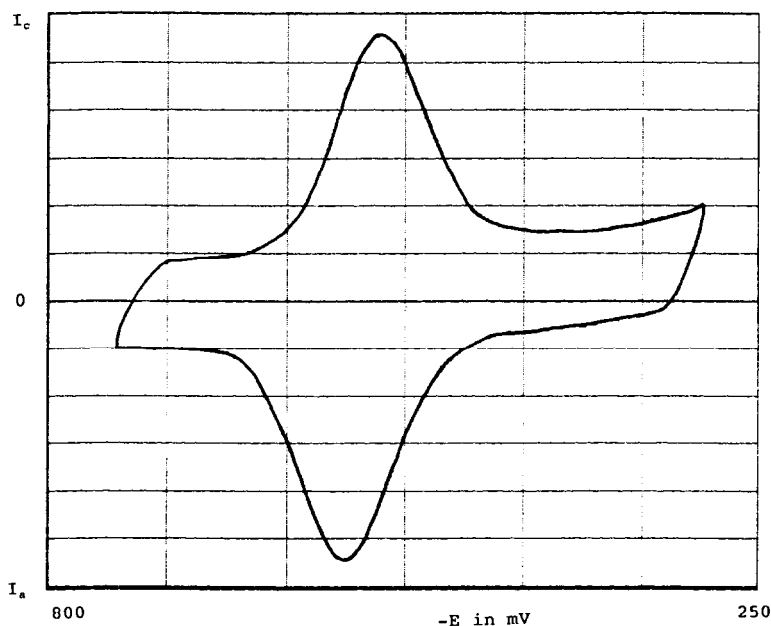
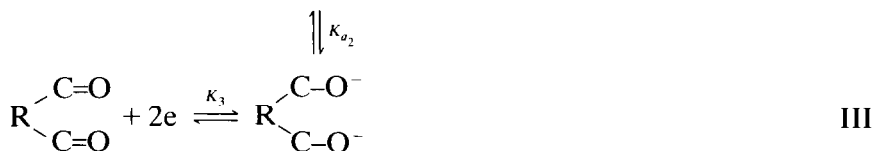
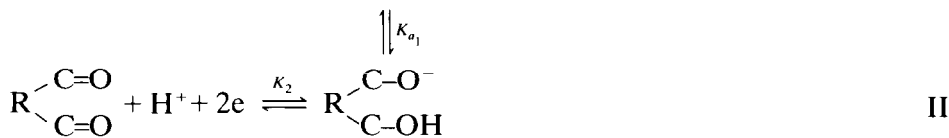
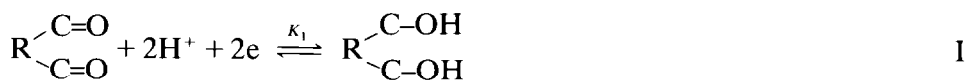


Fig. 2. Cyclic I - E curve for the electrode with thioindigo red C (pH = 13.8; $\nu = 10 \text{ mV s}^{-1}$).

Complete ionization of dye is achieved in alkaline medium. The redox properties of such systems can be characterized by the standard redox potential. We suggest that determination of the latter should be carried out using the method of cyclic voltammetry. Application of this method allows one to obtain the cyclic voltammograms, one of which is shown in Fig. 2. The I - E curve shown in Fig. 2 exhibits reversible anodic and cathodic peaks E_{I_a} and E_{I_c} . It is known [6] that in the case of cyclic voltammetry, the half-sum of the potentials of the anodic and cathodic peaks $E_{1/2} = 1/2(E_{pc} + E_{pa})$ can be used to define the standard redox potential of the “reversible” process. For this purpose, cyclic voltammograms of the dye

studied by us have been obtained over a wide pH region. The curves were processed on an IBM PC/AT computer using a specially developed programme which, taking into account the background curve, allows us to determine the position of the anodic and cathodic peaks, peak currents and the amount of electricity for redox reactions. The response of all $I-E$ curves obtained meets the requirements for Nernst's charge transfer [7], and the obtained linear dependence of $E_{1/2}$ on the acidity of the solution (Fig. 3) is, according to ref. 8, a direct consequence of the inclusion of proton concentration (reactivity), as the second co-item, in the second term of the Nernst equation

$$E = E^\ominus + \frac{2.3RT}{nF} \left(\lg \frac{O_s}{R_s} - m\text{pH} \right)$$

where O_s and R_s are the surface concentrations of the oxidized and reduced forms of the dye, respectively.

At $E = E_{1/2}$, $O_s = R_s$; then, $E_{1/2} = E^\ominus - (2.3m/nF)\text{pH}$, from which the standard redox-potential of the system is found easily.

The Nernst equation is given above in terms of the surface concentrations, since the redox transformations in the region of the peaks proceed in the adsorbed state. This is shown by the virtual insolubility of the initial dye and its leuco compound in water, by the equality of the amount of electricity for the anodic and cathodic processes (Table 1), and by the almost complete independence of this amount on the rate of change of potential (Table 2).

To check the technique suggested, an investigation was conducted on the well studied quinone–hydroquinone redox system, the standard redox potential for which is $E^\ominus = 699$ mV at 298 K [9]. Figure 3 shows the dependence of $E_{1/2}$ on the pH of the medium for this system. Data processing yields $E^\ominus = 695 \pm 7$ mV, slope 59 ± 1.2 mV; this is in good agreement with the literature data. Thus, this technique can also be used to obtain the quantitative characteristics of the redox behaviour of the vat dyes.

Figure 3 shows the dependence of $E_{1/2}$ values on pH of the medium for the dye thioindigo red C. The figure testifies to the linear character of the

TABLE 1

Amount of electricity Q for redox transformations at various pH values of medium ($v = 1 \text{ mV s}^{-1}$)

	pH						
	0.14	0.32	3.19	10.8	12.36	12.43	13.56
$Q_a/\mu\text{C}$	4.9	4.6	7.1	7.5	0.3	1.1	4.6
$Q_c/\mu\text{C}$	4.9	4.6	7.0	7.6	0.3	1.1	4.6

TABLE 2

Dependence of the amount of electricity (Q) for the redox transformations on the voltage sweep rate (v)

	pH							
	2.29				13.07			
v/mVs^{-1}	2	5	10	20	1	5	10	20
$Q_a/\mu\text{C}$	6.7	6.6	6.5	6.5	10.0	9.3	9.5	9.8
$Q_c/\mu\text{C}$	6.7	6.7	6.5	6.6	9.9	9.5	9.8	9.9

dependence. As can be seen, the straight line consists of three parts. In the intersection points, $[\text{H}^+] = K_1$ or K_2 , i.e. at these points, the numerical value of the pH of the solution is equal to the corresponding ionization constant ($\text{p}K$) [10]. Designation of the parts of the straight line in Fig. 3 corresponds to processes I, II and III in the scheme given previously. Data processing yields the following values of the standard potentials of the electrodic reactions: $E_{\text{I}}^{\ominus} = 294 \pm 8 \text{ mV}$; $E_{\text{II}}^{\ominus} = 87 \pm 7 \text{ mV}$; $E_{\text{III}}^{\ominus} = -228 \pm 11 \text{ mV}$; and the following values of the parameters of ionization constants: $\text{p}K_{a1} = 7.01$ and $\text{p}K_{a2} = 12.69$. The slopes of the linear parts of the straight line are as follows I, $57.6 \pm 1.2 \text{ mV}$; II, $29.6 \pm 1.7 \text{ mV}$; III, 0 mV . Using the data obtained, it is easy to determine the values of the change in free

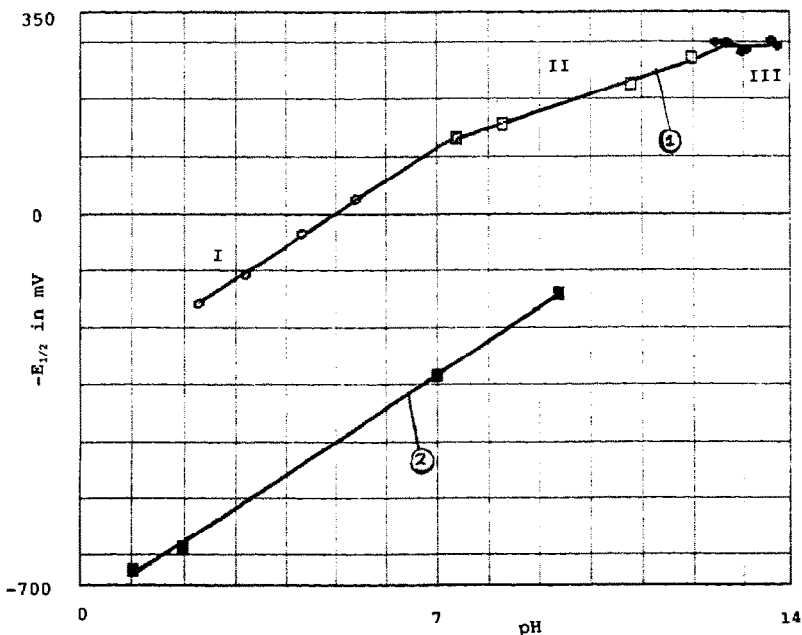


Fig. 3. Dependence of $E_{1/2}$ on pH of medium for thioindigo red C (1) and hydro-quinone (2).

energy of the electrochemical reaction: $-\Delta G = nFE^\ominus$. The following values (in kJ mol^{-1}) were obtained for the processes in the scheme: $\Delta G_{\text{I}}^\ominus = -56.8$; $\Delta G_{\text{II}}^\ominus = -16.8$; $\Delta G_{\text{III}}^\ominus = 55.6$; $\Delta G_{\text{a1}}^\ominus = 40.0$; $\Delta G_{\text{a2}}^\ominus = 72.3$. Earlier the values of $\text{p}K_{\text{a}}$ and E^\ominus for the vat dyes were obtained by spectrophotometric and redox titration of dye, which had been preliminarily reduced by sodium hydrosulphite, by oxidizer $-\text{K}_3\text{Fe}(\text{CN})_6$ in water, water–organic solvents (water–dioxane, water–pyridine) and pyridine [11–14]. However, in water only $\text{p}K_2$ values were obtained. The following values of the parameters of the ionization constants for thioindigo red C have been reported [14]: $\text{p}K_{\text{a1}} = 6.1$ in a 1:1 water–dioxane mixture; $\text{p}K_{\text{a2}} = 11.6$ in water.

However, it is noteworthy that the characteristics determined in organic solvents are used only to estimate the tendency to reduction in aqueous medium. The difficulties of obtaining meaningful results in aqueous medium relate to the slow operation of the electrodes and to insufficient reversibility of the system. Some of these problems occur due to the insolubility of the oxidized form, which can saturate the solution while precipitating at titration, or the precipitated oxidized dye can adsorb part of the reduced dye. The method proposed is free from these disadvantages and allows study of the behaviour of vat dyes in aqueous medium; this is especially important, since the application of this class of dyes relates to aqueous technology.

REFERENCES

- 1 T. Wickerstaff, *Physical Chemistry of Dyeing*, Gizlegprom, Moscow, 1956.
- 2 V.V. Budanov, I.N. Sokolova, N.E. Seredkin and B.N. Melnikov, *Izv. Vuzov. Khim. Khim. Tekhnol.*, 16 (1973) 1405.
- 3 U. Baumgarte, *Melliand Textilber.*, 51 (1970) 1332.
- 4 K.V. Lunyaka, Effective method of dyeing of viscose staple yarn by vat dyes on the base of purposeful change in the packing properties and state of dye, Ph.D. thesis, Kherson, 1982, 219 p.
- 5 M.I. Baznaov, *Izv. Vuzov. Khim. Khim. Tekhnol.*, 31 (1988) 62.
- 6 K.A.A. Askarov, B.D. Berezin, E.V. Bystritskaya et al., *Porphyrins: Spectroscopy, Electrochemistry, Application*, Nauka, Moscow, 1987.
- 7 M. Baser and H. Lund, *Organic Electrochemistry*, Vol. 1, Khimiya, Moscow, 1988.
- 8 B.B. Damaskin, *Electrode Processes in the Solutions of Organic Compounds*, MGU, Moscow, 1985.
- 9 V.V. Scorcelletti, *Theoretical Electrochemistry*, Khimiya, Moscow, 1970.
- 10 R.P. Yakimchuk, L.V. Mischenko and N.E. Bulusheva, *Application of Vat Dyes (Physico-Chemical Bases)*, Legprombytisdat, Moscow, 1985.
- 11 A.K. Gupta, *J. Chem. Soc.*, (1953) 3473, 3579.
- 12 W.J. Marshall and R.H. Petters, *J. Soc. Dyers Colour.*, 68 (1952) 289.
- 13 W.J. Marshall and R.H. Peters, *Bull. Inst. Text. Fr.*, 30 (1952) 415.
- 14 V.G. Abozin and V.V. Karpov, *Russ. J. Polym. Chem.*, 37 (1964) 880.