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Temperature Dependence of Physicochemical Characteristics of Redox Processes Involving Thioindigo Red C

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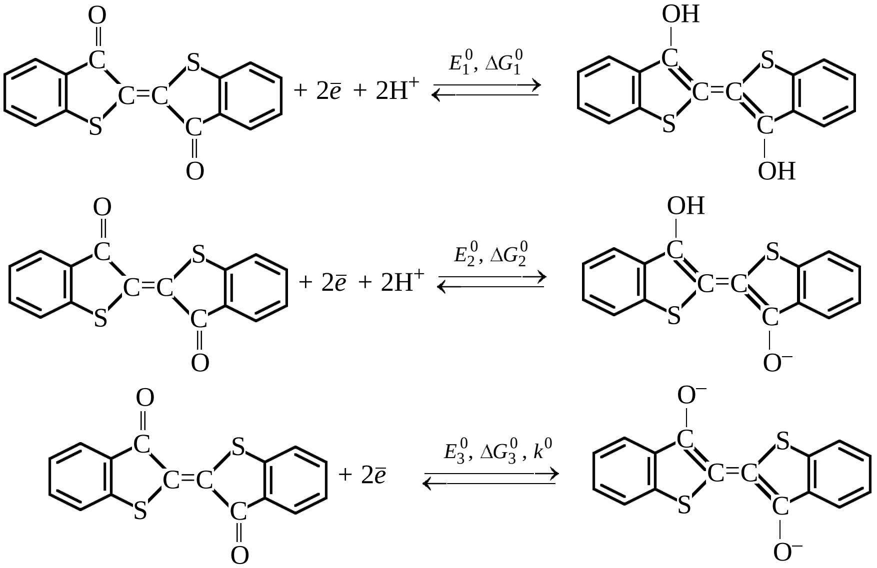
Abstract — Cyclic volammetry in water at 298–323 K was used to determine the thermodynamic and kinetic parameters of redox processes involving thioindigo red C. The resulting values were shown to depend on temperature and entropy.

Temperature is a factor that affects organic textile dyeing and allows controlling the process. The aim of the present work was to assess the effect of temperature on redox processes involving thioindigo red C which is one of the widely used vat dyes. The requisite of vat dyeing is reduction of the dyes. The reduction in aqueous media is a complicated reversible heterogeneous process which, depending on the pH of the medium, can be represented by the following scheme:



(1)

(2)

(3)

Earlier [1, 2] by cyclic volammetry we obtained the kinetic and thermodynamic characteristics of reactions (1)–(3). In the kinetic description of the most practically important reaction (3), two possible mechanisms have been taken into consideration: one-stage two-electron [Eq. (3)] and two consequtive one-electron stages I and II [Eq. (4)] similar to those well-studied with quinones [3, 4].

$$\mathrm{Dye} + \bar{e} \underset{\mathrm{I}}{\overset{k_{\mathrm{I}}^0}{\rightleftarrows}} \mathrm{Dye}^- + \bar{e} \underset{\mathrm{II}}{\overset{k_{\mathrm{II}}^0}{\rightleftarrows}} \mathrm{Dye}^{2-}. \qquad (4)$$

Here k^0, k_{I}^0, and k_{II}^0 are standard heterogeneous rate constants of the corresponding reactions, and Dye^- is the ionized form of the intermediate semiquinone.

The electrochemical measurements were performed

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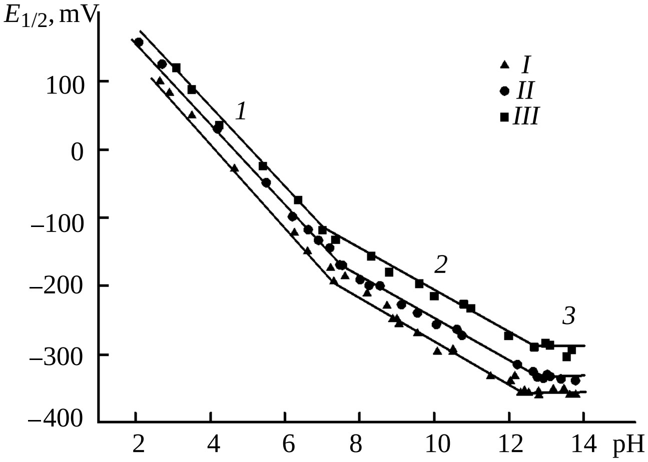
Table 1. Standard potentials E_i^0 and thermodynamic parameters of redox reactions (1)–(3) at various temperatures

Parameter	Reaction (1)			Reaction (2)			Reaction (3)		
	298 K	308 K	323 K	298 K	308 K	323 K	298 K	308 K	323 K
E_i^0, mV	294	285	272	87	56.65	36	–289	–334	–355
ΔG_i^0, kJ/mol	–56.8	–54.99	–52.48	–16.8	–10.99	–6.95	55.6	64.45	68.5
ΔH_i^0, kJ/mol	–108.0			–115.7			–93.4		
ΔS_i^0, J mol^{-1} K^{-1}	–172.3			–335.3			–504.9		

in cytrate–phosphate buffer solutions on a standard potentiostatic apparatus [1]. The working electrode was a carbon–graphite electrode made as described in [5]. The experimental procedure, purification of the dye, as well as treatment of cyclic voltammograms for calculating the thermodynamic and kinetic characteristics of the above processes have been described in [1, 2]. In the referred works we also showed that the responses of the cyclic voltammograms meet the Nernst charge-transfer conditions, and the redox reactions are reversible and involve sorbed dye. Corrections for temperature in calibrating the pH meter were introduced according to [6]. All reagents were of chemical or analytical grade. As reference we used a normal hydrogen electrode.

It is known [7, 8] that in cyclic volmammetry the half-sum of the anodic and cathodic peak potentials $E_{1/2} = 1/2(E_c + E_a)$ is almost equal to the standard redox potential of a reversible system (E^0), which is a measure of the free energy of the electrochemical reaction ($-\Delta G^0 = nFE^0$), and can be used for estimating the standard redox potential. The figure depicts the $E_{1/2}$–pH plots for 298, 308, and 323 K. As seen, the plots each have three linear portions *1*–*3*, and these portions relate respectively to the above three reactions. According to [7], the linear dependence of $E_{1/2}$ on the acidity of the medium for reversible electrode reactions involving protons directly follows from the fact that the proton concentration (activity) enters as the second factor into the second term of the Nernst equation: $E = E^0 + 2.3\ RT/(nF)[\log(\Gamma_o/\Gamma_r) - m\text{pH}]$, where Γ_o and Γ_r are the surface concentrations of the oxidized and reduced forms of the dye, respectively. When $E = E_{1/2}$, $\Gamma_o = \Gamma_r$, and $E = E^0 - 2.3\ m\text{pH}/(nF)$; thus the standard redox potential of the system is readily obtainable.



Plot of $E_{1/2}$ vs. pH for thioindigo red C for various temperatures. Temperature, K: (*I*) 323, (*II*) 308 K, and (*III*) 298. For (*1*)–(*3*), see text.

Tables 1 and 2 list the experimental data and the thermodynamic and kinetic characteristics of the above processes, estimated on their basis. The rate constants k_i^0 are averaged over 8–12 measurements. The rms deviation is 15–20%. The resulting ΔG_i^0 values are accurate to within 2–4%. The data in Table 1 were calculated from the temperature dependence of ΔG_i^0. As follows from Table 1, increased temperature favors reactions (1)–(3) ($\Delta\Delta G_i^0 > 0$). Reactions (1) and (2) are spontaneous, unlike reaction (3). As seen from Table 1, the enthalpy factor favors all the redox reactions in question. This factor varies only slightly in going from reaction (1) to reaction (2). The strongest effect is produced by the entropy factor. The negative values of the entropy (Table 1) show that the reactions involve ordering of the system. Increasing (in absolute value) entropy unfavors the reactions and prevents spontaneous occurrence of redox reaction (3) (Table 1). We suggest that the entropy is much contributed by solvation of the dye. It should therewith be noted that the fully ionized form of the dye [Eq. (3)] exerts a much stronger effect on the structurization processes than the molecular form [Eq. (1)] (Table 1).

The kinetic characteristics of reaction (3), too, are much temperature-dependent (Table 2). The acceleration of the reaction with increasing temperature is

Table 2. Rate constants of redox reaction (3), calculated for mechanisms (3) and (4)

T, K	Mechanism (3)		Mechanism (4)		
	k_{I}^0, s^{-1}	s	k_{I}^0, s^{-1}	k_{II}^0, s^{-1}	s
298	0.045	28.42	0.277	0.256	0.043
308	0.086	24.81	0.629	0.302	0.105
323	0.115	15.96	0.796	0.708	0.429

explained by lowering the energy barrier to the redox reaction. Moreover, the sum of the squared deviations from the regression line (s) shows that the increase in the temperature from 298 to 323 K does not change the mechanism of the redox reaction.

Our present data reveal a complex effect of the temperature on redox processes involving vat dyes. By further extending of the area of investigations (temperature, solvent composition, etc.) we can find conditions for the most effective control of these processes.

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