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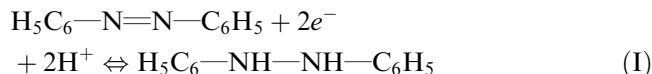
Voltammetry of azobenzene microcrystals

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Abstract Azobenzene solid particles have been mechanically attached to a graphite electrode and measured by cyclic staircase voltammetry. Well-developed and widely separated cathodic and anodic peaks were observed. Redox reaction is controlled by both the heterogeneous charge transfer kinetics and the mass transfer. Its mechanism is explained by the surface diffusion model. Reaction starts at the three-phase boundary, where electrons are transferred from the electrode surface to the attached azobenzene molecules. The electrons are then propagated over the surface of microcrystals by a series of exchange reactions between hydrazobenzene and azobenzene molecules, with the participation of proton donors from the solution. The apparent mass transfer occurs in this way. In the crystal lattice the transmission of protons is not possible, and consequently there is no propagation of electrons.

Introduction

Azobenzene and hydrazobenzene make a well-known redox couple [1–5]. In aqueous and alcoholic acidic electrolytes at a graphite electrode, their redox reaction includes practically simultaneous quasireversible transfer of two electrons and two protons



with a formal potential $E_f/V = 0.112 - 0.079 \text{ pH}$ [6, 7]. If $\text{pH} < 5$, electrogenerated hydrazobenzene undergoes irreversible reduction to aniline at potentials of 500 mV, or more negative than E_f of azobenzene reduction [8]. In aqueous acidic media, the first charge transfer of

azobenzene reduction is preceded by monoprotonization of azobenzene, whereas in alkaline media the charge transfer is followed by the protonization [1, 9]. The protonated azobenzene is reduced at more positive potentials than the unprotonated compound [8–10]. Both azobenzene and hydrazobenzene are strongly adsorbed at the graphite electrode surface [11]. A thick film of azobenzene monomers which have been crystallized at a glassy-carbon electrode surface is only partly electroactive. Its cyclic voltammogram consists of well-developed peaks, which are separated as widely as 500 mV at a scan rate of 20 mV/s [12, 13]. In this article, the redox reaction of azobenzene microcrystals is measured by abrasive stripping voltammetry, which is a new electroanalytical technique for the study of the electrochemical properties of solid materials [14–16]. The method is based on the mechanical transfer of solid particles to an electrode surface. A tip of paraffin-impregnated graphite rod is poisoned by pressing it gently into a small pile of pigment powder, and it is then directly used as a working electrode in voltammetric measurements [15, 17]. Azobenzene is not soluble in the cold water and remains immobilized at the electrode surface. This method has already been applied to several water-insoluble organometallic compounds which are insulators in the absence of liquid electrolytes [18–26]. A possible mechanism for this kind of solid-state redox reaction is proposed in this paper.

Experimental

Azobenzene (“Merck”, for synthesis), NaClO_4 , KNO_3 , NaOH and HClO_4 (all “Merck”, analytical grade) were used as received. Water was doubly distilled. Azobenzene was dissolved in the hot water, and a 10^{-3} M stock solution was prepared. The supporting electrolytes were 1 M NaClO_4 , 1 M HClO_4 and 1 M KNO_3 . The pH of the solutions was adjusted by the addition of citrate, borate and phosphate buffers.

The working electrode was a spectral-grade paraffin-impregnated graphite rod (diameter 5 mm, length 50 mm). Its clean and carefully polished circular surface was contaminated with traces of

solid azobenzene by pressing it into a small pile of azobenzene powder on a highly glazed ceramic tile and moving it with a circular motion for about 10 s. Alternatively, the clean and polished electrode surface was slightly roughened by an emery paper to increase its adhesion before being pressed into azobenzene powder. A platinum gauze was an auxiliary electrode, and Ag/AgCl/3M KCl (Metrohm) was the reference electrode ($E = 0.208$ V vs SHE).

Cyclic staircase measurements were performed using a multi-mode polarograph (Autolab, Eco Chemie, Utrecht), a personal computer and a printer. The potential step increment was 2.4 mV and the fraction of the step width at which the current was sampled was $\gamma = 0.35$.

Solutions were degassed with high-purity nitrogen for 30 min prior to the measurements. A nitrogen blanket was maintained thereafter. The working electrode was immersed in the electrolyte only during the voltammetric measurements. The cell was maintained at 20°C in a thermostat.

Results and discussion

Cyclic voltammograms of azobenzene which was abrasively transferred onto the slightly roughened surface of a graphite electrode in the acidic and basic 1 M KNO_3 solutions are shown in Fig. 1. They are very similar to the response of the thick film of azobenzene monomers [11–13]. The reduction and oxidation peaks are equally developed and widely separated. The peak currents increase with the repetitive cycling until a steady state is reached. If pH is increased, the response does not change significantly, except for the separation between the anodic and the cathodic peak potentials. At the scan rate of 2 mV/s, their formal potentials $E_f = (E_{P,a} + E_{P,c})/2$ depend linearly on the pH of solutions: $E_f/V = 0.10 - 0.06 \text{ pH}$, as can be seen in Fig. 2. In the acidic media, the cathodic peak potentials are a linear function of pH, with a slope of 125 mV/pH. This is shown in Fig. 3, and it indicates that a proton is involved in the rate-determining step of the reduction process. The anodic peak potentials depend on pH only in basic media.

Cyclic voltammograms of azobenzene microcrystals, which were immobilized on the highly polished surface of graphite electrode in the acidic 1 M NaClO_4 solution, are shown in Fig. 4. They are on average ten times smaller than the voltammograms which were obtained with the roughened electrode, but the change of the supporting electrolyte does not influence the form of the response. A small shoulder at about -0.2 V appears on the cathodic peaks in the first few scans and gradually vanishes with the repetitive cycling. Similar shoulders were observed in the cyclic voltammetry of the thick film of azobenzene [11–13]. Its origin is unknown.

Figure 5 shows that the peak potentials are linear functions of the logarithm of scan rates. The slopes of these relationships are 55 ± 15 mV for the anodic peaks and 80 ± 40 mV for the cathodic peaks.

Linear relationships between the logarithm of peak currents and the logarithm of scan rates are shown in Fig. 6. Their average slopes are 0.7 ± 0.1 , so the peak currents are $i_p = 3 v^{0.7 \pm 0.1}$ mA, on the roughened electrode, and $i_p = 0.25 v^{0.7 \pm 0.1}$ mA on the polished surface.

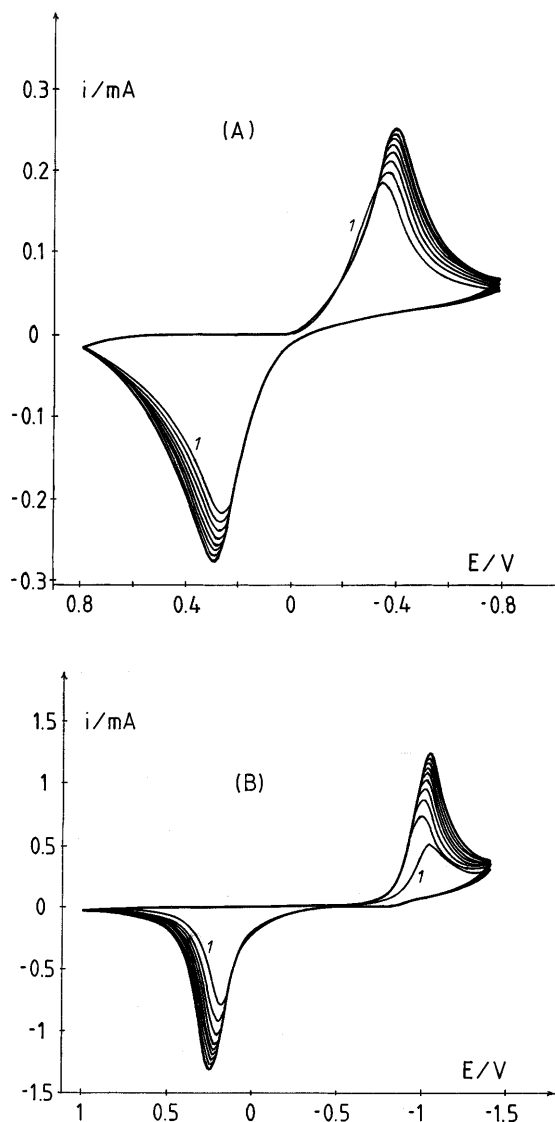


Fig. 1A, B Abrasive cyclic voltammetry of azobenzene microcrystals on slightly roughened paraffin-impregnated graphite electrode in 1 M KNO_3 , pH 2 (A) and pH 9 (B). $v = 100$ mV/s and $\Delta E = 2.4$ mV

Azobenzene is soluble in hot water. There is therefore a possibility that a small amount of azobenzene is dissolved from microcrystals at room temperature and adsorbed on the bare electrode surface. To investigate the origin of the response (whether it is the reaction of the microcrystals or of the adsorbed molecules only), a control measurement with dissolved azobenzene at a concentration of 2×10^{-5} M was performed. The results are shown in Fig. 7. The supporting electrolyte was 1 M NaClO_4 , pH 2 (HClO_4), and azobenzene was accumulated at the graphite electrode surface by adsorption at 0.4 V for 120 s. These cyclic voltammograms are 100 times smaller than the responses of microcrystals. Moreover, there is a significant difference in form between these two kinds of responses. This result indicates that in the abrasive stripping volta-

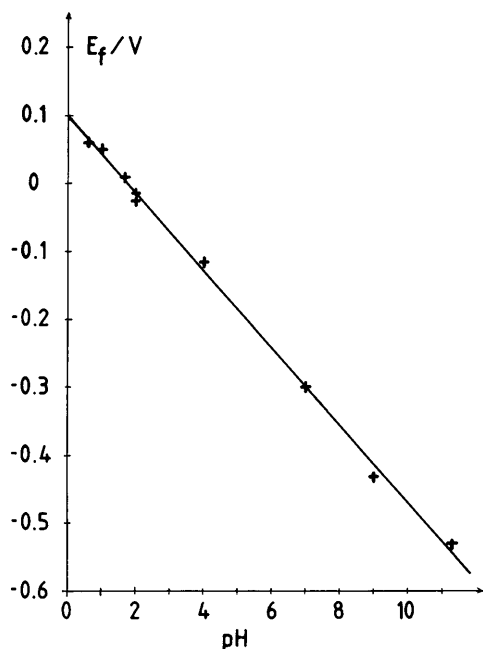


Fig. 2 Dependence of formal potentials of cyclic voltammograms of azobenzene microcrystals on pH of solutions. $v = 2$ mV/s

metry, the response originates from the redox reaction of the attached solid particles of azobenzene.

To explain these experiments, a certain mobility of either electrons or hydrazobenzene molecules on the surface of crystals has to be assumed. Roullier et al. [11–13] have proposed that the redox reaction of crystalline deposits of azobenzene includes an electrochemically induced dissolution of the solid, which is followed by a crystallization of the other form of the redox couple. A similar mechanism might be operative at the surface of the solid particle. Both azobenzene and hydrazobenzene are insulators, so there are no free electrons in the crystals. They are bound to covalent N-H bonds in hydrazobenzene. Furthermore, for reason of electroneutrality, the charge transfer to an azobenzene molecule which is attached to the electrode surface must be accompanied by the simultaneous protonation of the radical. However, in the crystal there are also no free protons. The only part of the solid particle where both electrons and protons are equally available is a three-phase boundary at which the electrode, the solution and the crystal meet. This long and irregular line surrounds many microcrystals which are directly attached to the electrode surface. Azobenzene molecules on this line can readily be reduced to hydrazobenzene. Because of different geometry, a hydrazobenzene molecule could be partly detached from the crystal of azobenzene without being fully dissolved. This would give it a surface mobility, and it could slide over the surface of the particle under the influence of the chemical potential gradient. By the surface diffusion of hydrazobenzene, new azobenzene molecules are continuously exposed to the solution at the three-phase boundary and immediately reduced. In the reverse scan,

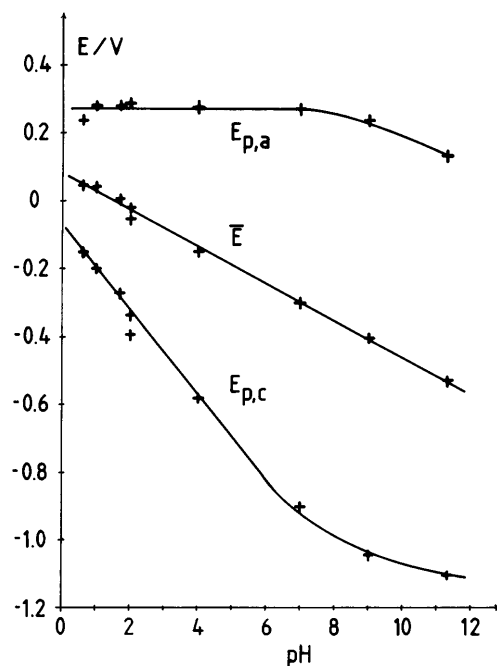


Fig. 3 Dependence of the cathodic and anodic peak potentials and the median potential of cyclic voltammograms of azobenzene microcrystals on pH of solutions. $v = 100$ mV/s

hydrazobenzene diffuses back towards the three-phase boundary where it is reoxidized and immobilized in the crystal lattice.

An alternative mechanism is proposed by Bond et al. [20, 21, 24, 26]. This is based on the concept of surface Faradaic conductivity [27]. If hydrazobenzene molecules are not mobile, the current can be conducted by a series of exchange reactions between the neighbouring redox sites. In acidic medium the reactions are:

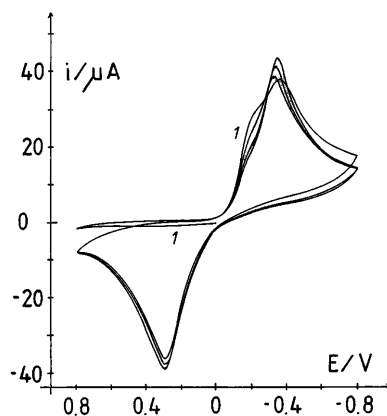


Fig. 4 Abrasive cyclic voltammetry of azobenzene microcrystals on highly polished paraffin-impregnated graphite electrode in 1 M NaClO_4 , pH 2 (HClO_4). $v = 50$ mV/s

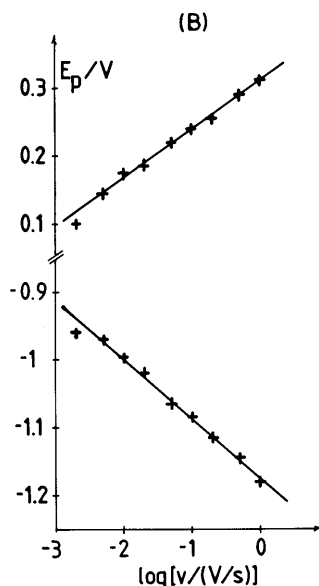
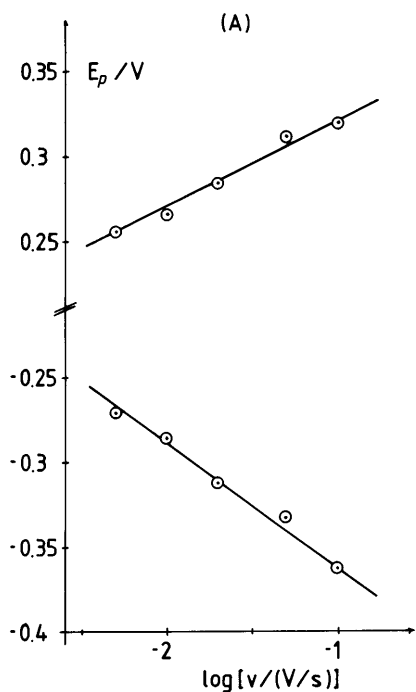
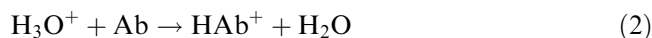


Fig. 5A, B Dependence of peak potentials of cyclic voltammograms of azobenzene microcrystals on the logarithm of scan rates, (A) 1 M NaClO₄, pH 2 and (B) 1 M KNO₃, pH 9

where Ab is azobenzene and H₂Ab is hydrazobenzene. It is assumed that azobenzene at the surface of the crystal is protonated by the mineral acid:



and that a doubly protonated azobenzene is the strongest proton donor:

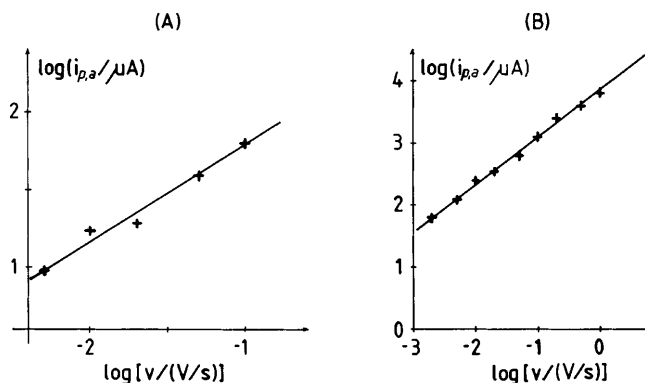
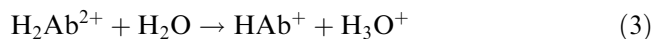
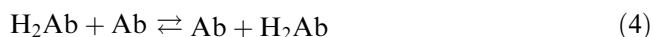
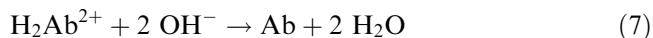
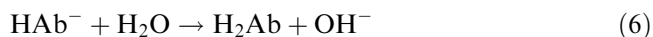


Fig. 6A, B Dependence of the logarithm of peak currents in cyclic voltammetry of azobenzene microcrystals on the logarithm of scan rates, (A) 1 M NaClO₄, pH 2 and (B) 1 M KNO₃, pH 9

In the neutral and basic solutions the reactions are:



It is assumed that both charge transfers are immediately followed by the protonations:



where Ab^{°-} is a symbol of a radical-anion. When the three-phase boundary is charged to the potential at which azobenzene molecules are reduced to hydrazobenzene, the chemical potential gradient is created and the electrons are propagated over the crystal surface by a series of exchange reactions (Eq. 1 or Eq. 4). Table 1 shows the reduction of ten molecules of azobenzene (0) and the subsequent reoxidation of hydrazobenzene (2) by the exchange reactions. The reoxidation starts at the three-phase boundary and not at the opposite end of the restricted surface as was erroneously suggested by Fig. 7 in [20].

In both mechanisms, the heterogeneous charge transfer reaction occurs only at the three-phase boundary where azobenzene and hydrazobenzene molecules are in the direct contact with the electrode surface and the solution. The rate of exchange reactions in the second mechanism determines the surface mobility of electrons and consequently the apparent mass transport. This can be seen from the general equation of linear diffusion [28]:

$$\partial c / \partial t = \partial (cuN^{-1} \partial \mu / \partial x) / \partial x \quad (8)$$

where c is the surface concentration in mol/cm², u is the mobility of the diffusing particle, $\mu = \mu^0 + RT \ln(a)$ is the chemical potential, $a = \gamma c$ is the surface activity, γ is the activity coefficient and N is Avogadro's number. Equation 8 can be transformed by the expansion $d \ln(a) = [d \ln(a) / d \ln(c)] d \ln(c)$. Using the relations

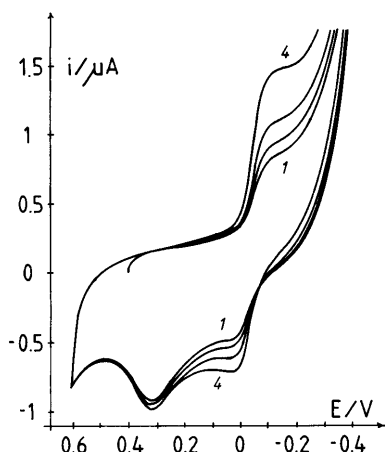


Fig. 7 Cyclic voltammetry of 2×10^{-5} M azobenzene solution in 1 M NaClO₄, pH 2 (HClO₄) which was preceded by the adsorptive accumulation of azobenzene on the surface of the paraffin-impregnated graphite electrode. $E_{\text{ads}} = 0.4$ V, $t_{\text{ads}} = 120$ s and $v = 50$ mV/s

$d \ln(\gamma c) = d \ln(\gamma) + d \ln(c)$ and $d \ln(c) = dc/c$, one obtains:

$$\partial c / \partial t = D \partial^2 c / \partial x^2 \quad (9)$$

where D is the coefficient of surface diffusion, which is proportional to the surface mobility [29]: $D = u RT[1 + d \ln(\gamma)/d \ln(c)]/N$. Thus, the mass transport on the surface of microcrystals can be mathematically described by Fick's second law of diffusion. Its solution depends on the geometry of crystals. The simplest geometry is an infinitely long triangular prism, as shown in Fig. 8. The prism lies with one of its sides on the electrode surface. Axis y is situated in one of two infinite three-phase boundaries, and the axis x lies in one of the free surfaces of the prism. This surface is finitely

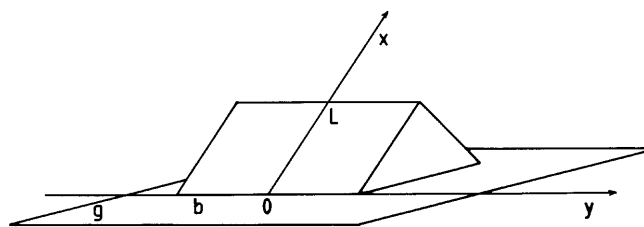


Fig. 8 A segment of an infinite triangular prism lying on the segment of an infinite electrode surface (g)

wide, its width being L . Redox reaction occurs at $x = 0$ and its product diffuses towards $x = L$. The prism is infinitely long to avoid edge effects. In this way, the problem of mass transport is reduced to one-dimensional planar diffusion in the finite space. Thus, Eq. (9) has to be solved for the following initial and boundary conditions.

$$t = 0, 0 \leq x \leq L : c_{\text{ox}} = c^*, c_{\text{r}} = 0 \quad (10)$$

$$t > 0, 0 \leq x \leq L : c_{\text{ox}} + c_{\text{r}} = c^* \quad (11)$$

$$(\partial c_{\text{r}} / \partial x)_{x=0} = i/nFbD \quad (12)$$

$$(\partial c_{\text{r}} / \partial x)_{x=L} = 0 \quad (13)$$

$$i/nFb = k_s \exp(-\alpha \vartheta) [(c_{\text{ox}})_{x=0} - (c_{\text{r}})_{x=0} \exp(\vartheta)] \quad (14)$$

$$\vartheta = nF(E - E^0)/RT \quad (15)$$

where c_{ox} and c_{r} correspond to azobenzene and hydrazobenzene, respectively, b is the length of three-phase boundary, k_s is the standard rate constant of redox reaction, α is the transfer coefficient, E is the electrode potential, E^0 is the standard potential, and i is the current.

The solutions of Eqs. 9 and 15 for linear scan voltammetry [30, 31] and staircase voltammetry [32] were found in the literature on thin-layer cells.

The theory predicts that the currents in cyclic voltammetry depend on the dimensionless diffusion space $L(v/D\Delta E)^{1/2}$ and the kinetics parameter $k_s(\Delta E/Dv)^{1/2}$, where ΔE is the potential increment in staircase voltammetry and v is the scan rate. If $k_s(\Delta E/Dv)^{1/2} < 10^{-2}$, the peak currents depend linearly on the scan rate if $L(v/D\Delta E)^{1/2} < 1$, and on the square root of scan rate if $L(v/D\Delta E)^{1/2} > 10$. Also, the slope of the linear relationship between the peak potentials and the logarithm of the scan rate is equal to $RT/\alpha nF$ in the first case and $RT/2\alpha nF$ in the second. The experimentally observed relationship $i_p = Kv^x$, where $x = 0.7 \pm 0.1$, can be explained as an average response of redox reactions on many different crystal surfaces, some very small and others much wider. Such composite responses are characterized by an average slope of the linear relationship between peak potentials and the logarithm of scan rate: $\partial E_p / \partial \log v = xRT/\alpha nF$, where again $x = 0.7 \pm 0.1$. By applying this equation to the experimental data, the parameters $\alpha n = 0.6 \pm 0.1$ and

Table 1 The propagation of hydrazobenzene (2) by the exchange reactions on the restricted crystal surface consisting of ten molecules of azobenzene (0) and the reoxidation of the surface

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$\beta n = 0.8 \pm 0.1$ were calculated. This result is in agreement with the observed dependence of cathodic peak potentials on pH, and it indicates that one proton is involved in the rate-determining step of the reduction process. On the basis of the separation between the cathodic and anodic peaks, this simple model suggests that $k_s D^{-1/2} = 5 \times 10^{-5} \text{ s}^{-1/2}$ at pH 2, but for the detailed kinetic analysis a more elaborate model is needed.

Finally, regarding the possibility that the redox reaction can be propagated through the crystal lattice, this can be ruled out. Roullier et al. [11] gave evidence that there is no direct transmission of electrons between neighbouring reduced and oxidized sites in the crystal. This means that the exchange reaction (Eq. 4) is not possible without the participation of water as both proton donor and proton acceptor. In the solid state the necessary transfer of protons cannot occur. However, it is not possible to establish definitely the redox reaction mechanism of azobenzene microparticles solely on the basis of voltammetric measurements. In this paper it is demonstrated that the mass transport can be explained by the mobility of electrons on the surface of azobenzene microcrystals. The proposed electron exchange reactions between immobilized azobenzene and hydrazobenzene molecules cause the apparent surface diffusion process which is equivalent to the real diffusion of hydrazobenzene molecules. The mathematical model of assumed transport phenomenon is developed. Regardless of which species (electrons or molecules) are mobile, the heterogeneous charge transfer which is controlled by the redox kinetics takes place only at the three-phase boundary, and the mass transfer is possible only on the crystal surface. The expansion of the redox reaction into the volume of particles would require the mobility of both electrons and protons, but the exchange of protons between immobilized hydrazobenzene and azobenzene molecules in the solid state seems to be improbable.

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