

THE FENTON REACTION AT POLARIZED LIQUID/LIQUID INTERFACES: KINETIC ANALYSIS

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In the present work we deal with the properties of the Fenton reaction at the interface, which should initiate polymerization of suitable monomers by providing hydroxyl radicals in a highly controllable manner. For the purposes of our study and for subsequent application, the reactants, i.e., ferrous ion and hydrogen peroxide, must be separated by the liquid interface in order that the reaction be driven by electrochemically controlling the transfer of one reactant across the interface into the liquid phase containing the other reactant. The Fenton reaction takes place in the aqueous phase and hydrogen peroxide is a hydrophilic, electrically neutral compound; consequently, it is necessary to find an electrically charged compound of divalent iron that would be soluble in the organic phase and could be transferred from the organic into the aqueous phase at a suitable potential difference across the liquid/liquid interface. Certain derivatives of ferrocene meet these demands and we have found in preliminary experiments that the (ferrocenylmethyl)trimethylammonium cation (TMFc⁺) is most convenient. Ferrocene is transferred into the aqueous phase and the reaction, in which the OH^{*} radicals are produced and ferrocene is oxidized, takes place in the aqueous phase and then the non-oxidized and oxidized ferrocene is transported back to the organic phase yielding two reverse peaks on cyclic voltammogram. Rate of the overall reaction can be controlled electrochemically, by controlling the ferrocene transport across the interface by the applied potential difference [1].

The rate constant of the homogeneous reaction involved in such a reaction system can be determined by cyclic voltammetry, employing the ratio of the heights of the reverse and forward peak currents of the reactant [2]. However, a more general approach is to determine the rate constant from the equality of the heights of the voltammetric peaks corresponding to the transfer of the reactant and of the reaction product back from the aqueous phase into the organic phase. The cyclic voltammogram and the reaction scheme is depicted in Fig. 1. The shape of this voltammogram depends on the relative rates of polarization and of the homogeneous chemical reaction; at a given rate of the chemical reaction, increasing rate of polarization ν leads to a progressive decrease in peak 2, i.e., the effect of the chemical reaction on the voltammogram progressively decreases.

An analysis and general solution of this problem lead for the condition $i_{p1}=i_{p2}$ to the dimensionless rate constant $\kappa(E_{12})=RTka^*/(F\nu)$, where k is the homogeneous rate constant and a^* is the initial concentration of A [3]. The results are summarized in Table 1.

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References

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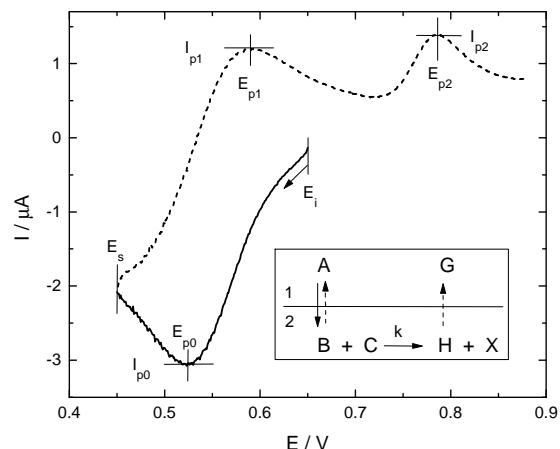


Fig. 1. A schematic representation of the cyclic voltammogram and of the reaction scheme. E_i – initial potential, E_s – reversal potential, E_{p0} , I_{p0} – the forward peak (transfer of the reactant from phase 1 to phase 2), E_{p1} , I_{p1} – the reverse peak (transfer of the reactant back from phase 2 to phase 1), E_{p2} , I_{p2} – peak corresponding to transfer of the reaction product from phase 2 to phase 1. The cyclic voltammogram was recorded in the system consisting of: 0.01 mol l⁻¹ Na₂SO₄, 0.005 mol l⁻¹ H₂SO₄ (pH 2), 0.001 mol l⁻¹ H₂O₂ and 0.1 mol l⁻¹ acrylonitrile in the aqueous phase; 0.005 mol l⁻¹ TBACBB and 5x10⁻⁴ mol l⁻¹ TMFcCBB in 1,2-dichloroethane. CBB is [7,8,9,10,11,12-Br₆-1-CB₁₁H₆]. For the experimental details see ref. [1]. Polarization rate is 5 mV s⁻¹.

Table 1

The important characteristics of the reaction system computed from the experimental data [1] whose examples are given in Fig. 1.

$E_{p0} + 0.028 - E_s / V$	0.101
$E_{p2} - E_{p1} / V$	0.194
E_{12} / V	0.214
κ	0.0209
$\nu / [V/sec]$	0.005
$k / [dm^3/(mol.s)]$	8.1

Notes:

The first row contains the absolute value of the difference of E_s potential and the standard potential of the first transfer reaction, the second row is the peak potential difference, the third row is the value of the standard potential difference for the second and the first transfer reaction, the fourth row is the dimensionless rate constant, the fifth row is the rate of polarization and the last row is the calculated rate constant from the dimensionless rate constant.