

## ELECTRON TRANSFER BETWEEN FERROCENE AND HEXACYANOFERRATE(III) ACROSS THE WATER/1,2-DICHLOROETHANE INTERFACE

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Kinetics of electron transfer between ferrocene or its derivative (1,1'-diethyl- or 1,1'-distearylferrocene) in dichloroethane and hexacyanoferrate(III) in water was studied by means of convolution potential sweep voltammetry. Within the accessible range of experimental conditions no effect of either the potential or concentrations of reactants on the rate constant of electron transfer from the organic to the aqueous phase ( $k^{o \rightarrow w} = 1 \cdot 10^{-7} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$ ) was observed. Electron transfer was shown to occur far from the potential range, in which the ferricenium ion transfer can take place. However, the reaction was complicated by the chemical decomposition of ferricenium in dichloroethane ( $k = 0.346 \text{ s}^{-1}$ ).

A large class of chemical reactions, whose kinetics has been studied extensively, is that of oxidation-reduction (redox) reactions<sup>1</sup>. At present both theoretical<sup>2</sup> and practical<sup>3</sup> aspects of homogeneous as well as heterogeneous redox reactions have received a great deal of interest. Redox reactions play a key role in chemical-to-electrical or solar-to-electrical energy conversions. Those occurring in living systems deserve particular attention<sup>3</sup>.

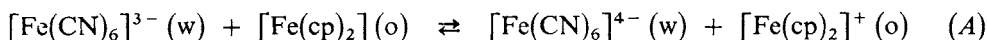
Ferrocene-ferricenium redox couple has been used to advantage as a model redox system. Up to the present, its homogeneous reactions have been studied with hexacyanoferrate(III) (ref.<sup>4</sup>), Pt(IV) complexes<sup>5</sup>, iodine<sup>6</sup>, clathrate cobalt chelates<sup>7</sup>, and Fe<sup>3+</sup> cation<sup>8</sup>. As regards heterogeneous reactions, electrochemical behaviour of ferrocene<sup>9</sup> as well as its use in preparation of chemically modified electrodes<sup>10</sup> should be noted. Recently, the attention has focused on reactions of ferrocene in microheterogeneous systems<sup>11,12</sup>.

The interface between two immiscible electrolyte solutions represents an important model system. Various methods, which are analogous to those used in classical studies on electrode kinetics<sup>13,14</sup>, have been developed and applied to examine its properties and reactions located here, namely polarography with electrolyte dropping electrode<sup>13</sup>, cyclic voltammetry<sup>15</sup> and chronopotentiometry<sup>16</sup>.

Two electron transfer reactions occurring at the boundary between two immiscible liquids have been reported in literature. As the first one, the reaction between hexa-

cyanoferrate(III) in the aqueous phase and 1,1'-dibutylferrocene in dichloroethane was examined, in which case the organic phase formed an artificial membrane located between two aqueous phases<sup>17</sup>. The second reaction of this type is that between hexacyanoferrate(III) and ferrocene at the water/nitrobenzene interface<sup>18-20</sup>.

The aim of this work was to study kinetics and mechanism of the reaction



at the interface between water (w) and 1,2-dichloroethane (o).

## EXPERIMENTAL

### Chemicals

Symmetric 1,1'-substituted ferrocenes of general formula  $[\text{Fe}(\text{cp-R})_2]$ , where cp denotes cyclopentadienyl and R = Cl, COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, were prepared as described in literature<sup>21-23</sup>. The substituent R = COC<sub>17</sub>H<sub>35</sub> was introduced by means of Friedel-Crafts acetylation of ferrocene with stearoylchloride in dichloromethane in the presence of aluminium trichloride as a catalyst<sup>24</sup>.

Ferricenium salts of general formula  $[\text{Fe}(\text{cp})_2]\text{X}$ , with X =  $[\text{ClO}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{FeCl}_4]^-$ , and  $[\text{B}(\text{C}_6\text{H}_5)_4]^-$ , were prepared as solids by adapting the procedure described in literature<sup>25</sup>. Except for tetraphenylborate, other salts are stable in the air, provided that they have been desiccated thoroughly. Ferricenium tetraphenylborate decomposes slowly even though the salt has been desiccated quickly and carefully and has been kept under vacuum or the inert gas. Therefore, only freshly prepared compound has been always used.

The aqueous phase was prepared from double distilled water and LiCl (puriss., p.a., Fluka AG) as a base electrolyte. For the preparation of the non-aqueous phase 1,2-dichloroethane (puriss., p.a., Fluka AG) was used as received. Tetrabutylammonium tetraphenylborate (TBATPB) and crystal violet tetraphenylborate (CVTPB), both prepared by adapting the procedure described in literature<sup>26</sup>, and tetraphenylarsonium 3,3'-*como*-bis(undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate(1-)) (TPADCC) prepared by Dr. K. Baše (Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences) as described elsewhere<sup>27</sup>, were used as base electrolytes of the non-aqueous phase.

Ferrocene, i.e. bis( $\eta$ -cyclopentadienyl)iron(II) or  $[\text{Fe}(\text{cp})_2]$ , was purchased from BDH Chemical Ltd. and resublimated prior to use.

Acetonitrile, which was used as a solvent in voltammetric measurements, was purified by fractional distillation from a mixture with phosphorus pentoxide<sup>28</sup>. In all operations the solvent was handled by using the technique of Schlenk flasks<sup>29</sup>.

All other chemicals were purchased from Lachema, Brno (Czechoslovakia).

### Apparatus

Electrolytic vessel for cyclic voltammetry at the interface between two immiscible electrolyte solutions<sup>30</sup> as well as the four-electrode potentiostatic circuit<sup>15</sup>, supplemented with the positive feedback loop<sup>31</sup> has been already described. The interface established in the vessel had an area of  $10 \cdot 2 \cdot 10^{-6} \text{ m}^2$ . The scheme of the galvanic cell formed in the vessel can be described as

Ag|AgCl| 0.05 mol dm<sup>-3</sup> LiCl, w||0.05 mol dm<sup>-3</sup> TBATPB, o|| 0.05 mol dm<sup>-3</sup> TBACl, w|AgCl| Ag.

In order to extend the usable potential range towards more negative potentials in some measurements, TBATPB was replaced by TPADCC or CVTPB and the reference electrode for the non-aqueous phase was filled with the aqueous solution of the corresponding chloride. In case that CVTPB was used, the latter reference electrode was connected to the cell by means of a salt bridge containing a common anion.

The potential difference  $E$  of the galvanic cell above is the Galvani potential difference between the aqueous (w) and the non-aqueous (o) phase defined as

$$\Delta_o^w \varphi = \varphi(w) - \varphi(o),$$

which is related to the formal potential difference for the reference ion  $\Delta_o^w \varphi_{\text{REF}}^0$  (REF = TBA<sup>+</sup>, TPA<sup>+</sup> or CV<sup>+</sup>), i.e.

$$E = \Delta_o^w \varphi - \Delta_o^w \varphi_{\text{REF}}^0.$$

Values of  $\Delta_o^w \varphi_{\text{REF}}^0$  in the water/1,2-dichloroethane system can be found in literature<sup>32</sup>.

The available potential range, where the measurements of the charge transfer can be carried out, is cut off by transfer reactions of quaternary cation or counter anion at negative or positive potentials, respectively. Most measurements were performed with TBATPB. In measurements involving substitution derivatives of ferrocene an extended potential range was required and, therefore, TPADCC or CVTPB was used instead.

By convention, the electric current flowing through the galvanic cell above, which is connected with the transfer of a negative charge from the organic to the aqueous phase, is considered as positive<sup>33</sup>.

Voltammetric measurements on a rotating platinum disc electrode were conducted with an apparatus described previously<sup>34</sup>. All electrochemical experiments were performed at 25°C with solutions prepared in the air (except for those involving acetonitrile as a solvent).

## RESULTS AND DISCUSSION

### *Kinetics of Electron Transfer Between Ferrocene and Hexacyanoferrate(III) Across the Water|1,2-Dichloroethane Interface*

Figure 1 shows the voltammogram of base electrolytes. The potential range where no transfer of base electrolyte ions is observed (so-called potential window) takes up to about 0.26 V. An addition of ferrocene to 1,2-dichloroethane does not cause any change in the shape of the curve 1. An addition of potassium hexacyanoferrate(III) to the aqueous solution of the base electrolyte makes the potential window only slightly narrow due to a shift in its positive limit towards more negative values. The shift is connected with the difference in the formal potential of Li<sup>+</sup> and K<sup>+</sup> ions, the latter being less positive. In case that potassium hexacyanoferrate(III) and ferrocene are present in the aqueous and non-aqueous phase, respectively, both positive and negative currents rise above their background values, cf. the corresponding cyclic voltammogram in Fig. 1 (curve 2).

The value of the peak potential difference  $\Delta E_p = E_p^+ - E_p^- \geq 0.080$  V, it exceeds considerably that predicted by the theory of a reversible and diffusion-controlled ion transfer<sup>14</sup>. Moreover, this quantity depends on concentrations of reactants in both phases, specifically  $\Delta E_p$  increases when reactants' concentrations decrease.

Peak current values  $I_p^+$  and  $I_p^-$  are in this case lower than one would expect for a reversible and diffusion-controlled transfer of an ion (e.g. picrate) having equal concentration<sup>30</sup>. The ratio  $I_p^+/I_p^-$  is close to one for scan rates  $v$  above  $0.1$  V s<sup>-1</sup>. On decreasing the scan rate,  $I_p^+/I_p^-$  drops steeply, as can be seen from Fig. 2. The plot of  $I_p^+$  vs the square root of  $v$  gives a straight line with the zero intercept, which fits formally in the Randles-Ševčík equation for a diffusion-controlled process. On the other hand,  $I_p^-$  exhibits a non-linear dependence on  $v^{1/2}$ .

Since the solution of the transport problem for the electron transfer between reactants whose transport is governed by the linear diffusion has not been reported yet, the kinetic parameters we evaluated with the help of the convolution analysis<sup>35</sup>. Its essential advantage consists in that the quantitative evaluation of voltammetric data can proceed without specifying the type of function, which determines the potential dependence of the rate constant. As a matter of fact, it is the rate constant that is inferred from experiment as a function of the potential by means of this analysis.

Convolution voltammograms were evaluated from single-sweep current vs potential curves measured with the equilibrated solutions. The  $m$ - $E$  curve of the electron transfer between the redox couple O1/R1 in the aqueous phase ( $c_{O1}^0 \neq 0$ ,  $c_{R1}^0 \neq 0$ ) and the redox couple O2/R2 in the organic solvent phase ( $c_{O2}^0 = 0$ ,  $c_{R2}^0 \neq 0$ ) is described by the following equation

$$\frac{(m_{d,O1} - m)(m_{d,R2} - m)}{(m_{d,R1} + m)m} = \frac{I \cdot m_{d,O1}m_{d,R2}}{nFAk^{o \rightarrow w} c_{O1}^0 c_{R1}^0 (m_{d,R1} + m)} + (D_{R1}D_{O2}/D_{O1}D_{R2})^{1/2} \exp[-nF(E - E^0)/RT], \quad (1)$$

where the limiting convolution current  $m_{d,i} = nFAD_i^{1/2}c_i^0$ ,  $n$  is the number of electrons transferred from 1,2-dichloroethane to water,  $A$  is the interfacial area,  $E^0$  is the formal potential of electron transfer,  $D_i$  is the diffusion coefficient, which was determined by voltammetry at the rotating platinum disc electrode<sup>36</sup>,  $c_i^0$  is the bulk concentration of reactant and  $I$  is the current corresponding to electron transfer which was read from the voltammogram. In our measurements no hexacyanoferrate(II) was present in the solution bulk and hence  $c_{R1}^0 = 0$  and thereby  $m_{d,R1} = 0$ . When  $E \rightarrow \infty$  the convolution current reaches a limiting value, which is either  $m_{lim} = m_{d,O1}$  (for  $m_{d,O1} \leq m_{d,R2}$ ) or  $m_{lim} = m_{d,R2}$  (for  $m_{d,R2} \leq m_{d,O1}$ ). The concentration of ferrocene in 1,2-dichloroethane was many times higher than that of hexacyanoferrate(III) in the aqueous phase, so that  $m_{lim} = m_{d,O1}$ .

Curve 1 in Fig. 3 shows the potential dependence of the convolution current  $m$ . Contrary to expectations, the experimental values of  $m_{d,i}$  showed a non-linear dependence on the concentration. At higher concentrations of hexacyanoferrate(III) the experimental value of  $m_{d,i}$  was about half as the corresponding theoretical one. The latter, however, was used in calculations.

FIG. 1

Cyclic voltammogram of electron transfer across the water/1,2-dichloroethane interface. Scan rate:  $0.05 \text{ V s}^{-1}$ , initial potential  $E_i = 0.15 \text{ V}$  1 Base electrolytes: aqueous phase,  $0.05 \text{ mol dm}^{-3} \text{ LiCl}$ ; non-aqueous phase,  $0.05 \text{ mol dm}^{-3} \text{ TBATPB}$  in 1,2-dichloroethane. 2 Electron transfer reaction: aqueous phase, base electrolyte +  $6.7 \cdot 10^{-4} \text{ mol dm}^{-3}$  potassium hexacyanoferrate(III); non-aqueous phase, base electrolyte +  $0.1 \text{ mol dm}^{-3}$  ferrocene

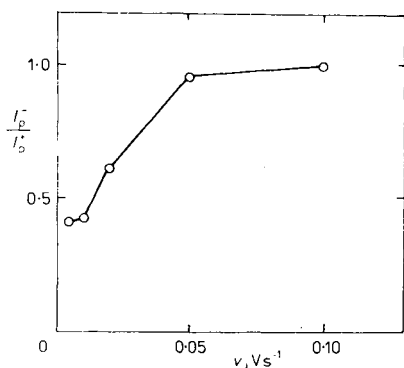
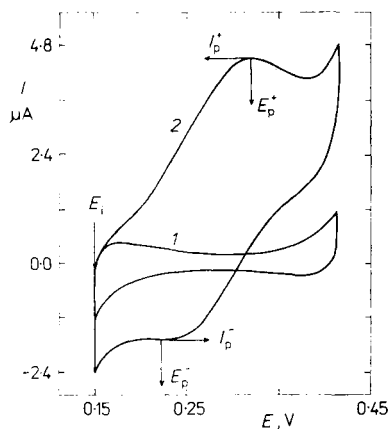


FIG. 2

Plot of the peak current ratio vs the scan from the cyclic voltammogram of the electron transfer across the water/1,2-dichloroethane interface

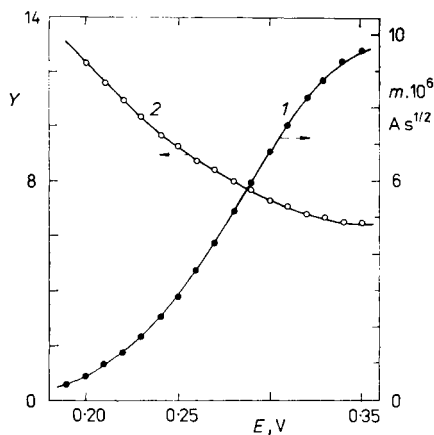


FIG. 3

Plot of the convolution current  $m$  and the logarithmic function  $Y$  vs the applied potential. For composition of phases see legend to Fig. 1, curve 2. Scan rate:  $0.05 \text{ V s}^{-1}$  1 Convolution current  $m$ ; 2 the function  $Y$

In case of a diffusion-controlled electron transfer ( $k^{o \rightarrow w} \rightarrow \infty$ ), the first term on the r.h.s. of Eq. (1) approaches zero and the logarithmic analysis, i.e. the plot of logarithm of the r.h.s. of Eq. (1) ( $\equiv Y$ ) vs the potential  $E$ , should give a straight line with a slope of  $RT/nF$ . In case of electron transfer occurring between hexacyanoferrate(III) and ferrocene across the water/1,2-dichloroethane interface, such a behaviour was observed only at low potentials, as one can see from Fig. 3 (curve 2), but the slope of the linear part was only 2/3 of that expected for a reversible process, irrespective of reactants' concentrations and sweep rate. Formal potential  $E^0 = 0.430$  V was inferred by using the suggested procedure<sup>20</sup>. The latter value was used further in calculations.

The reaction (A) at the water/1,2-dichloroethane interface was quasi-reversible till irreversible even under conditions that the analogous reaction at the water/nitrobenzene interface appears to be as reversible<sup>20</sup>.

Kinetic data for the reaction (A) can be obtained with the help of Eq. (1). In this way the rate constant  $k^{o \rightarrow w} = 1 \cdot 10^{-7} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$  was evaluated for the electron transfer between ferrocene in 1,2-dichloroethane and hexacyanoferrate(III) in water. The constant was independent of both the potential  $E$  and the concentration ratio  $c_{R2}/c_{O1} = \langle 100-400 \rangle$ . As compared with the analogous reaction occurring at the water/nitrobenzene interface<sup>20</sup>, the rate constant is lower. It is to be stressed also that the logarithmic analysis gives the non-Nernstian slope, which points to a more complex reaction mechanism at potentials below 0.3 V, or to the interference with another process on a single scan.

#### *Mechanism of Electron Transfer between Ferrocene and Hexacyanoferrate(III) across the Water/1,2-Dichloroethane Interface*

The overall reaction between ferrocene in 1,2-dichloroethane and hexacyanoferrate(III) in water is described by Eq. (A). The transfer of ferricenium cation across the water/nitrobenzene interface was shown to occur at potentials more negative than those characteristic for the electron transfer<sup>37</sup>. At the water/1,2-dichloroethane interface the ferricenium ion transfer is observed at even somewhat more negative potentials, with the formal potential difference  $\Delta_o^w \varphi^0 = -0.038$  V and the corresponding value of  $\Delta G_{ir}^{o, w \rightarrow o} = -3.7 \text{ kJ mol}^{-1}$ . The ferricenium ion transfer is obviously well separated from the electron transfer of Eq. (A).

An important factor, which affects the mechanism of the electron transfer reaction is the stability of reactants involved. Low stability of ferricenium ion in neutral and basic aqueous solutions is well known<sup>38</sup>. It has been shown that ferricenium decomposes rapidly even in 1,2-dichloroethane or nitrobenzene solutions, whereas it is relatively stable in acetonitrile. Kinetics of this decomposition, which was measured with the help of the rotating platinum disc electrode, is that of a first-order reaction with the rate constant  $k = 0.346 \text{ s}^{-1}$  (in the presence of  $0.05 \text{ mol dm}^{-3}$

TBATPB) depending on the nature of the organic base electrolyte present. Earlier investigations showed that, in contrast to other quarternary cations, ferrocene is oxidized spontaneously in non-aqueous solutions when tetraphenylarsonium cation is present<sup>37</sup>.

The fast decay of ferricenium concentration is manifested by the asymmetry of current peaks (cf. Fig. 2) on one hand, and by the shift of the half-wave potential of the convolution voltammogram on the other hand. Both effects depend on the magnitude of the rate constant of the chemical reaction in the EC mechanism<sup>39</sup>.

On the basis of available information, Eq. (A) supplemented with that describing the follow-up chemical decomposition of ferricenium seems to give a good picture of the redox reaction followed here. However, other mechanisms cannot be excluded, in particular those involving at least one ion transfer step, which can be hardly distinguished from the mechanism above, provided that all equilibria are completely mobile.

With respect to the catalytic effect of cations on both homogeneous<sup>40</sup> and heterogeneous<sup>41</sup> redox reactions of hexacyanoferrate(III), the bridge mechanism of electron transfer appears to be a quite probable route.

#### *Substitution Derivatives of Ferrocene in the Reaction (A)*

The very fact<sup>42</sup> that sensitivity of ferrocene derivatives towards the oxidation correlates with the nature of the substituent on the cyclopentadienyl ring triggered an extensive study, which has revealed the existence of the linear relationship between the redox potential and the Hammett constant  $\sigma_p$  of substitution derivatives of ferrocene. In a previous communication<sup>20</sup>, the formal potential of the electron transfer reaction at the interface between two immiscible electrolyte solutions was described by the equation

$$\Delta_o^w \varphi = E_{O_2/R_2}^0 - E_{O_1/R_1}^0 \quad (2)$$

This equation makes it possible to predict which ferrocene derivatives should undergo the electron transfer reaction in the potential range available. Though this prediction was favourable for 1,1'-distearoylferrocene ( $E_{1/2} = 0.540$  V at the rotating platinum disc electrode in 1,2-dichloroethane containing  $0.05 \text{ mol dm}^{-3}$  TBATPB as a base electrolyte), its oxidation by hexacyanoferrate(III) at the water/1,2-dichloroethane interface was not detected. Then 1,1'-diethylferrocene ( $E_{1/2} = 0.437$  V under the same conditions as above) was the only derivative, whose reaction was measurable voltammetrically when CVTPB was used as the organic base electrolyte. The behaviour of this system was quite analogous to that involving the non-substituted ferrocene, and the corresponding electron transfer rate constant was the same within the plausible range of experimental error.

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