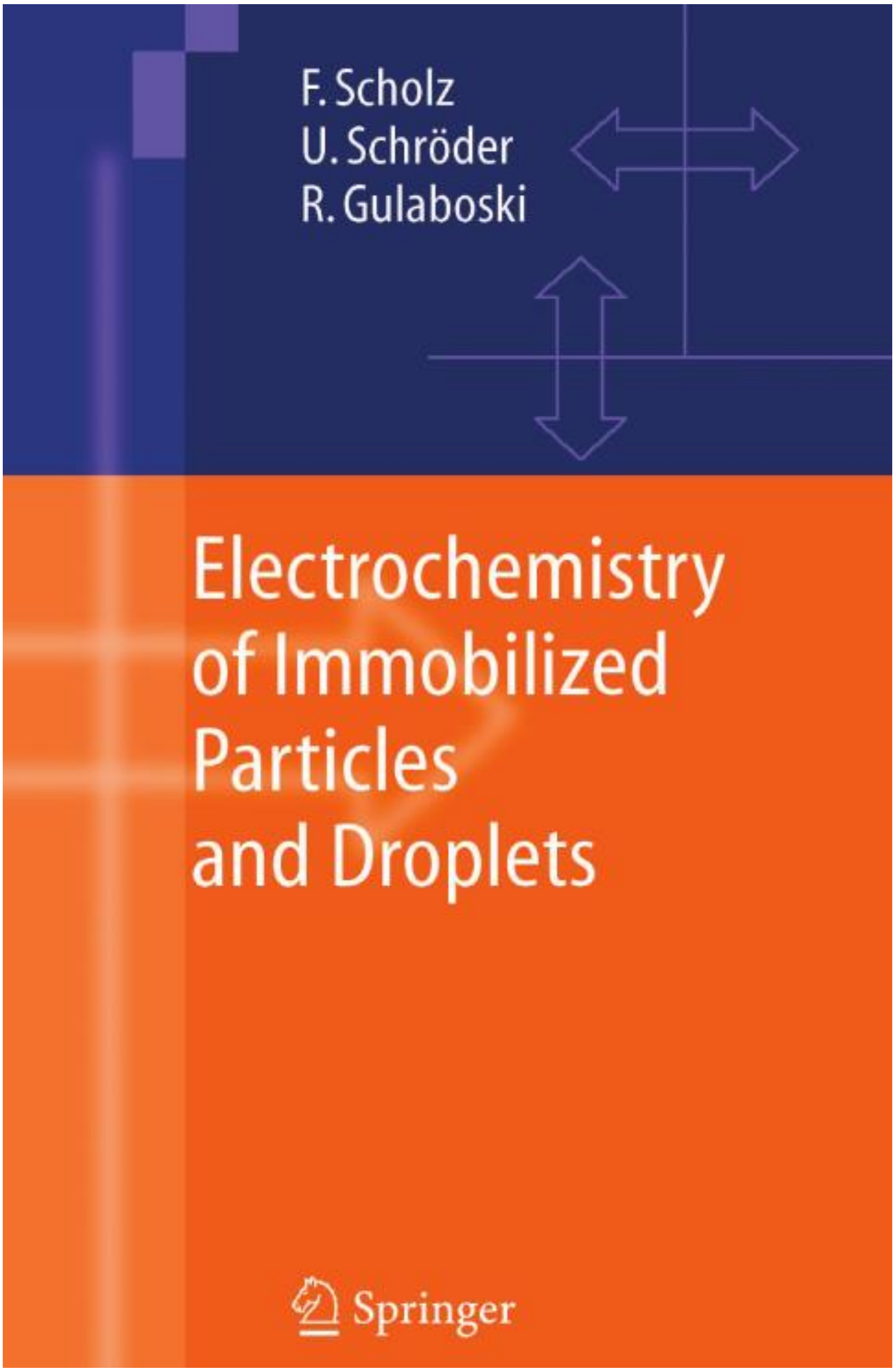
Voltammetry of Redox Compounds Dissolved in Organic Solvents- Ion Transfer Processes Across Liquid-Liquid Interfaces

Fritz, Scholz, Rubin Gulaboski in the book “Electrochemistry of Immobilized Particles and Droplets”



6.2 The Electrochemistry of Compounds Dissolved in Droplets

The electrochemistry of electroactive compounds dissolved in water immiscible solvents and attached to the surface of solid electrodes in the form of droplets is an interesting topic. This chapter, will be focused on one feature of such electrodes, namely the *ion transfer* between the adjacent liquid phases, which always accompanies the electron transfer between the solid electrode and the electroactive compound. Figure 6.22 schematically depicts the situation at the electrode when a droplet of a solution of an electroactive compound is attached to an electrode surface. Very similar to the situation of immobilized solid particles that are undergoing insertion electrochemical reactions (see, for example, the electrochemistry of metal hexacyanoferrates in previous chapters), and even more similar to the situation of immobilized electroactive droplets (Chapter 6.1) one can observe a reaction scenario that could be called "insertion electrochemistry with droplets". This approach offers a unique access to the standard Gibbs energy of ion transfer across a liquid | liquid interface [B 132].

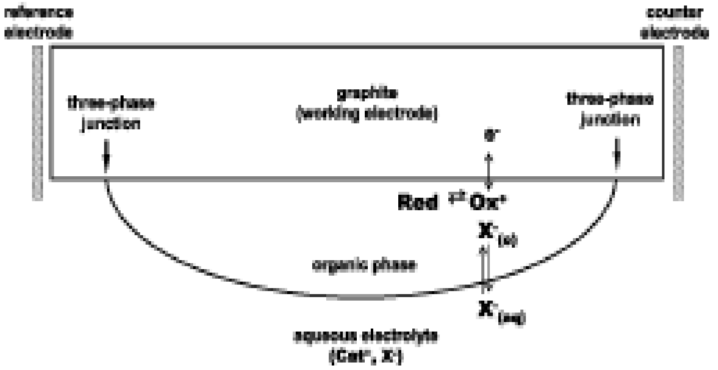


Fig. 6.22. Three-phase electrode consisting of a droplet of an organic solvent containing an electrochemically oxidizable compound Red. The droplet adheres to a solid electrode (graphite) and it is immersed in an aqueous electrolyte solution. The oxidation of Red at the graphite-organic liquid interface is accompanied by a transfer of X^- from aqueous to the organic phase [B 280]

The standard Gibbs energy of ion transfer between two solvents is an important thermodynamic quantity since its value portrays the difference between the free energies of solvation of an ion i in two solvents α and β. The standard Gibbs energy of ion transfer from phase α to phase β ($\Delta G_{\alpha,\ i}^{\beta\ \circ}$) is related to the standard potential of ion transfer ($\Delta\phi_{\alpha,\ i}^{\beta\ \circ}$), and to the standard partition coefficient (P_i) through the following equations:

$$\Delta\phi_{\alpha,\ i}^{\beta\ \circ} = \frac{-\Delta G_{\alpha,\ i}^{\beta\ \circ}}{z_i F} \tag{6.6}$$

$$P_i = \exp\left(\frac{-\Delta G_{\alpha,\ i}^{\beta\ \circ}}{RT}\right) \tag{6.7}$$

The logarithm of the partition coefficient (log*P*) is a measure of the liphophilicity of compounds. It helps understanding a variety of biological phenomena, such as passive transfer through membranes, enzyme-receptor interactions, drug activities, etc., and it is a major parameter in quantitative structure activities relationships (QSAR) and quantitative structure properties relationships (QSPR) [7]. While log*P* of neutral compounds is relatively easily accessible by different partition techniques, such as shake-flask methods, partition chromatography, high-performance liquid chromatography, extraction [1], etc., log*P* of single ions was accessible until recently only by four-electrode voltammetry at the interface of two immiscible electrolyte solutions (ITIES) [8]. The inevitable presence of electrolytes in the two immiscible solvents, as well as the non-polarizability of some important water | organic solvent interfaces [9] severely restricts the use of that technique.

In this chapter the applicability of the three-phase electrode approach for determining standard Gibbs energies of transfer of ions will be discussed. To achieve an ion transfer across the organic droplet|aqueous solution interface, a small amount of a neutral electroactive compound is dissolved in an organic and water-immiscible solvent that is devoid of any electrolyte. A droplet (e.g., 1 µL) of that solution is attached to the surface of a suit-

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[7] Testa B, van de Waterbeemd H, Folkers G, Gay R (2001) Pharmacokinetic Optimization in Drug Research. Wiley-VCH, Weinheim

[8] Girault HHJ, Schiffrin DJ (1989) Electrochemistry of liquid-liquid interfaces. In: Bard, AJ (ed) Electroanalytical Chemistry, A Series of Advances. vol 15. Dekker, New York, pp 1-141

[9] Marcus Y (1997) Ion Properties. Dekker, New York

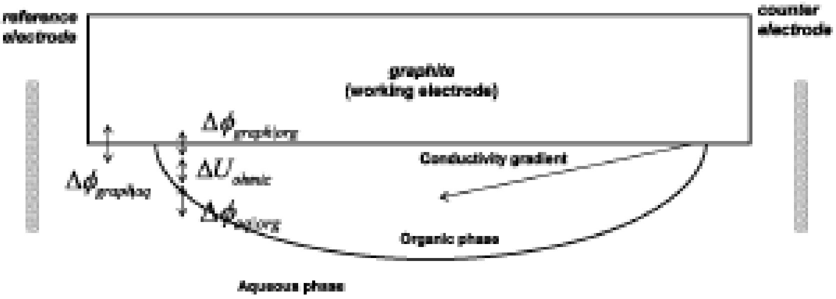

Fig. 6.23. Potential drops at three-phase electrode (details see text) [B 280]

able electrode. Graphite electrodes (e.g., PIGE) are superior compared to metal electrodes because the stability of the attachment of a nonaqueous droplet is very good. The electrode with the attached droplet is immersed in an aqueous electrolyte solution of the salt Cat^+A^-. In this solution the reference and counter electrodes are placed as in a conventional voltammetric cell. A prerequisite for the proper operation of the experiment is the existence of the *three-phase junction line* where the three phases working electrode, organic solution, and aqueous solution boarder to each other. Since no electrolyte is added to the organic solvent, the initial conductivity in the region near the edge of the droplet results only from free partition of the salt present in the aqueous solution. The applied potential between the working and the reference electrode can initially act in a restricted area only, i.e., at the three-phase junction where all three phases meet. Figure 6.23 depicts the potential drops at such a three-phase electrode.

The potential drop at the graphite | organic phase interface is given by the following expression:

$$\Delta\phi_{\mathrm{graph|org}} = \Delta\phi_{\mathrm{graph|aq}} - \Delta U_{\mathrm{ohmic}} - \Delta\phi_{\mathrm{aq|org}} \tag{6.8}$$

The potential drop $\Delta\phi_{\mathrm{graph|aq}}$ at the interface graphite electrode | aqueous solution in Eq. 6.8 is controlled potentiostatically. However, the potential drop $\Delta\phi_{\mathrm{graph|org}}$ at the interface graphite | organic solution is in fact the applied potential difference ($\Delta\phi_{\mathrm{graph|aq}}$) diminished (i) by the value of the ohmic drop $\Delta U_{\mathrm{ohmic}}$ inside the organic phase, and (ii) by the value of the potential drop $\Delta\phi_{\mathrm{aq|org}}$ (i.e., the potential drop due to the partition of ionic species) at the interface aqueous solution | organic solution. Indeed, the value of $\Delta\phi_{\mathrm{aq|org}}$ will be different for different ions that are initially present in the aqueous phase. Consequently, the potential $\Delta\phi_{\text{graph|org}}$ will be altered in the same way as the nature of the ions in the aqueous phase is changed. When the organic droplet does not contain any deliberately added electrolyte ΔU_{ohmic} will be very large all over the graphite | droplet interface with the only exception of the very edge, i.e., the three-phase junction region. A thin layer that is situated at the droplet-water interface will acquire a higher ionic conductivity due to salt partition from the aqueous phase. Therefore, an electrochemical oxidation of Red (see Fig. 6.22) can start without ohmic impediment only in that three-phase junction region. The ohmic drop will decrease within the droplet with progressing of the electrode reaction because Ox^+ and X^- are ions that provide ionic conductivity (the concentration of Red is usually rather high, e.g., higher than 10^{-2} M).

The *electron transfer* process occurring at the electrode | organic phase interface is *necessarily coupled* to a *transfer of ions* across the aqueous phase | organic phase interface in order to maintain the electroneutrality of the organic phase. In voltammetric experiments, both the electron and ion transfer processes are recorded together. The nature of the ion transfer takes place, i.e., the transfer of anions from water to the organic phase or the transfer of electrochemically created cations from the organic phase to water, depends primarily on the ratio of the standard Gibbs energies of ion transfer of both candidates. Generally, if the solvation of the electrochemically created cations Ox^+ in the organic phase is stronger than the hydration of the anions in the aqueous phase X^-, then a transfer of anions from the aqueous phase to the organic phase will take place, as depicted in the Fig. 6.22.

A *transfer of cations* from aqueous phase to the organic phase can be achieved if the solvation of electrochemically generated anions in the organic phase, created by reduction of a neutral electro-reducible compound present in the organic phase, is stronger than the hydration of the cations in the aqueous phase.

In both cases the standard Gibbs energies of ion transfer can be deduced from the formal potentials of cyclic or square-wave voltammograms (or of any other voltammetric technique), following the algorithm described next.

According to Fig. 6.22, the overall reaction proceeding at a microdroplet-modified electrode can be written as follows:

$$\text{Red}_{(o)} + \text{A}^-_{(aq)} \rightleftarrows \text{Ox}^+_{(o)} + \text{A}^-_{(o)} + \text{e}^- \qquad \text{(XIV)}$$

If no kinetic constraints exist with respect to the electron and ion transfer, the thermodynamic treatment applied to Reaction XIV leads to the following form of the Nernst equation:

$$E = E^{\ominus}_{\mathrm{Ox}^+_{(o)}/\mathrm{Red}_{(o)}} + \Delta\phi^{\mathrm{o}\ \ominus}_{\mathrm{aq},\ \mathrm{A}^-} + \frac{RT}{F}\ln\frac{a_{\mathrm{Ox}^+_{(o)}}\, a_{\mathrm{A}^-_{(o)}}}{a_{\mathrm{Red}_{(o)}}\, a_{\mathrm{A}^-_{(aq)}}} \tag{6.9}$$

In Eq. 6.9 E is the applied potential between the working and the reference electrode, $E^{\ominus}_{\mathrm{Ox}^+_{(o)}/\mathrm{Red}_{(o)}}$ is the standard potential of the redox couple $\mathrm{Ox}^+/\mathrm{Red}$ in the organic solvent, $\Delta\phi^{\mathrm{o}\ \ominus}_{\mathrm{aq},\ \mathrm{A}^-}$ is the standard potential of transfer of anions from the aqueous phase to the organic phase, $a_{\mathrm{Ox}^+_{(o)}}$ and $a_{\mathrm{Red}_{(o)}}$ are the activities of the oxidized and reduced forms of the electroactive compound in the organic phase, while $a_{\mathrm{A}^-_{(o)}}$ and $a_{\mathrm{A}^-_{(aq)}}$ are the activities of anions in the organic phase and aqueous solutions, respectively. In a first approximation, the activities in the Nernst equation have been replaced by concentrations. Since the concentration of the anions in the aqueous phase does not change significantly during the experiment, Eq. 6.9 can be rewritten as:

$$E = E^{\ominus}_{\mathrm{Ox}^+_{(o)}/\mathrm{Red}_{(o)}} + \Delta\phi^{\mathrm{o}\ \ominus}_{\mathrm{aq},\ \mathrm{A}^-} - \frac{RT}{F}\ln c_{\mathrm{A}^-_{(aq)}} + \frac{RT}{F}\ln\frac{c_{\mathrm{Ox}^+_{(o)}}\, c_{\mathrm{A}^-_{(o)}}}{c_{\mathrm{Red}_{(o)}}} \tag{6.10}$$

Electroneutrality requires that

$$c_{\mathrm{Ox}^+_{(o)}} = c_{\mathrm{A}^-_{(o)}} \tag{6.11}$$

The mass conservation law in respect to the organic phase leads to

$$c_{\mathrm{Red}_{(o)}} + c_{\mathrm{Ox}^+_{(o)}} = c^*_{\mathrm{Red}_{(o)}} \tag{6.12}$$

where $c^*_{\mathrm{Red}_{(o)}}$ is the initial concentration of the oxidizable compound in the organic phase. When the applied potential equals the formal potential of the redox pair it follows that

$$c_{\mathrm{Red}_{(o)}} = c_{\mathrm{Ox}^+_{(o)}} \tag{6.13}$$

By substitution of Eqs. 6.11-6.13 in Eq. 6.10 allows calculating the formal potential ($E^{\ominus'}_{\mathrm{c}}$) of the system:

$$E_{c}^{\ominus'} = E^{\ominus}_{\mathrm{Ox}^{+}_{(o)}/\mathrm{Red}_{(o)}} + \Delta\phi^{\mathrm{o}\,\ominus}_{\mathrm{aq},\,\mathrm{A}^{-}} - \frac{RT}{F}\ln c_{\mathrm{A}^{-}_{(aq)}} + \frac{RT}{F}\ln\frac{c^{*}_{\mathrm{Red}_{(o)}}}{2} \qquad (6.14)$$

Since the voltammetric systems obtained by these experiments, at least with the used redox probes, possess all features of electrochemical reversibility and the transfer coefficients are obviously near to 0.5, it is reasonable to take the mid-peak potentials of cyclic voltammograms as the formal potential of the system.

The last equation shows that the formal potential of the voltammograms depends on the *nature of the anions in aqueous phase* (via the values of $\Delta\phi^{\mathrm{o}\,\ominus}_{\mathrm{aq},\,\mathrm{A}^{-}}$). Generally, the more lipophilic the anions are, the more negative is the value of $\Delta\phi^{\mathrm{o}\,\ominus}_{\mathrm{aq},\,\mathrm{A}^{-}}$. Consequently, the oxidation of the compound Red in the organic phase will occur at more negative potentials (i.e., it will be easier oxidized) as the lipophilicity of the transferable anions increases. Further, the formal potential should shift by about 59 mV in negative direction for a ten-fold increase of the concentration of the transferable anions in aqueous phase. This criterion, taken together with the stability of the voltammograms recorded during consecutive cycling serves as an important indicator for the reversibility of the processes occurring at the droplet-modified electrodes.

When an *electroreducible* compound is dissolved in the organic phase, then its reduction at a three-phase electrode can provoke the transfer of cations from water to the organic phase. This can be described by the following reaction:

$$\mathrm{Ox}_{(o)} + \mathrm{Cat}^{+}_{(aq)} + e^{-} \rightleftarrows \mathrm{Red}^{-}_{(o)} + \mathrm{Cat}^{+}_{(o)} \qquad (\mathrm{XV})$$

Analogously to the previous case, the thermodynamic treatment of Reaction XV leads to the following Nernst equation, which is valid when cations are transferred from the aqueous to the organic phase:

$$E_{c}^{\ominus'} = E^{\ominus}_{\mathrm{Ox}_{(o)}/\mathrm{Red}^{-}_{(o)}} + \Delta\phi^{\mathrm{o}\,\ominus}_{\mathrm{aq},\,\mathrm{Cat}^{+}} + \frac{RT}{F}\ln c_{\mathrm{Cat}^{+}_{(aq)}} + \frac{RT}{F}\ln\frac{2}{c^{*}_{\mathrm{Ox}_{(o)}}} \qquad (6.15)$$

The more lipophilic the cations present in the aqueous phase are, the more positive will be $\Delta\phi^{\mathrm{o}\,\ominus}_{\mathrm{aq},\,\mathrm{Cat}^{+}}$. Subsequently, the reduction of the organic compound Ox in the oil phase will occur at more positive potentials as the lipophilicity of the cations in the aqueous phase increases. The formal potential of the coupled electron/ion reaction at the three-phase electrode will shift by 59 mV in positive direction for a ten-fold increase of the concentration of the transferable cations in the aqueous solution.

6.2.1 The Determination of Standard Gibbs Energies of Transfer of Anions

The oxidation of a neutral lipophilic organic compound dissolved in an organic solvent is a precondition for transferring anions across the aqueous | organic interface. The compound decamethylferrocene (dmfc) (bis(pentamethylcyclopentadienil)iron(II)) possesses that ability (see Fig. 6.24). It is a lipophilic compound, soluble in various organic solvents, but almost insoluble in water [10]. It exhibits an electrochemically reversible one electron redox reaction in organic solvents and it is commonly used as a reference standard for potential in measurements in nonaqueous media [4]. The oxidation of dmfc in a droplet of nitrobenzene (NB) attached to an electrode and immersed in aqueous solutions of different sodium salts gives rise to well-defined square-wave voltammograms, the formal potentials of which are sensitive to the nature and concentrations of the anions present in the aqueous solutions (see Fig. 6.25). Of course, in principle, any voltammetric measuring technique can be applied, however, square-wave voltammograms offer a simple way to measure the formal potential as it is the peak potential of the signals. The overall electrode process pro-

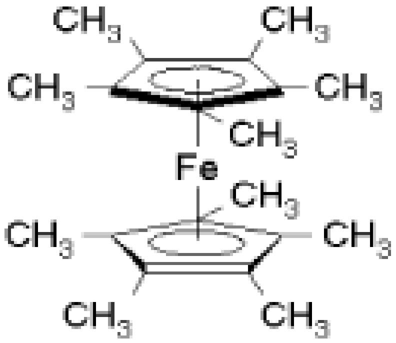

Fig. 6.24. Structure of decamethylferrocene (dmfc)

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[10] Noviandri I, Brown KN, Fleming DS, Gulyas PT, Lay PA, Masters AF, Philips L (1999) J Phys Chem B, 103:6713-6722

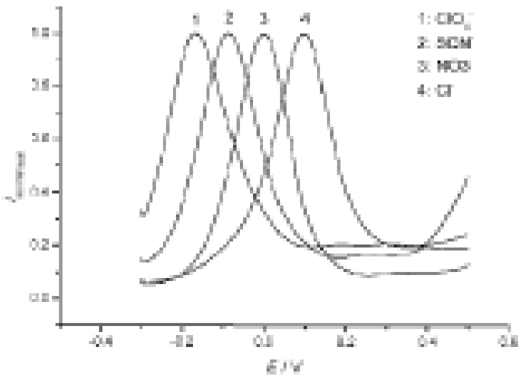

Fig. 6.25. Normalized square-wave voltammograms recorded at electrodes modified with droplets of a dmfc solution in nitrobenzene (0.1 M) and immersed in 1 M aqueous solutions of different sodium salts. The instrumental parameters were: frequency (f) of 100 Hz, amplitude (E_{sw}) of 50 mV, and scan increment (dE) of 0.15 mV

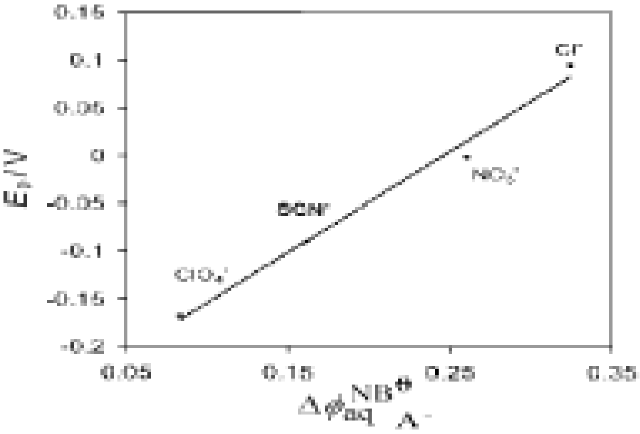

Fig. 6.26. Dependence of the formal potentials of the square-wave voltammograms depicted in Fig. 6.25 on the standard potentials of transfer of anions across the water nitrobenzene interface [B 240]

ceeding at the three-phase electrode can be written as follows:

$$\text{dmfc}_{(NB)} + \text{A}^-_{(aq)} \rightleftarrows \text{dmfc}^+_{(NB)} + \text{A}^-_{(NB)} + 1\text{e}^- \qquad \text{(XVI)}$$

The dependence of the formal potentials of the square-wave voltammograms (Fig. 6.25) on the standard potentials of transfer of the anions from water to nitrobenzene is linear and characterized by a slope of 0.95 and an intercept of -0.259 mV (cf. Fig. 6.26). The slope of this dependence is near to 1, just as predicted by Eq. 6.14. From the intercept of this dependence one can evaluated the standard potential of the couple dmfc$^+$/dmfc in nitrobenzene which reads -0.184 V (vs. Ag/AgCl, saturated KCl). This value

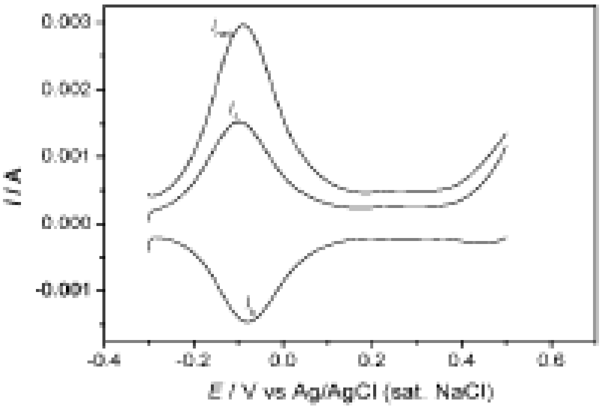

Fig. 6.27. Forward (I_f), backward (I_b) and net (I_{net}) components of a square-wave voltammetric response of a nitrobenzene droplet containing 0.1 M dmfc attached to the surface of the working electrode and immersed in 1 M aqueous solution containing SCN^- anions. The experimental conditions were: frequency f = 100 Hz, amplitude Esw = 50 mV, and scan increment dE = 0.15 mV [B 240]

can be also determined by common measurements in the non-aqueous phase in the presence of a reference standard.

Knowing the value of the standard potential of $dmfc^+$/dmfc in nitrobenzene, and studying the oxidation of nitrobenzene solution of dmfc at a droplet-modified electrode which is immersed in aqueous solutions containing different anions, one can estimate the standard potentials of transfer (and thus the standard Gibbs energies of transfer) of the anions from water to nitrobenzene using Eq. 6.14. To identify the electrode system to follow Reaction XVI, one can use the dependence of the formal potentials on the logarithm of concentration of anions in the aqueous phase, and the stability of the voltammetric responses during consecutive cycling.

The electrochemical reversibility of the electrode process should be checked by studying the dependence of the formal potentials on the frequency (in square-wave voltammetry) or on the scan rate (in cyclic voltammetry). Representative square-wave voltammogram of all current components of the electrode process of dmfc obtained at a three-phase electrode with coupled transfer of thiocyanate anions is given in Fig. 6.27.

This approach has been utilized for the determination of the standard Gibbs energies of transfer of a large number of inorganic anions [B 132, 206, 240, 259] as well as of various organic anions, such as the anions of aliphatic and aromatic carboxylic acids [B 240, 259], substituted phenols [B 240, 269], drugs [B 269], and amino acids and peptides [B 262, 266]. As organic phases the common solvents nitrobenzene and dichloroethane

[B 132, 240, 259, 262, 266] have been used. Remarkably, also *n*-octanol [B 206, 269], nitrophenyl octyl ether [B 282], and D- and L-menthol [B 221] have been exploited as organic solvents. Some of the data of lipophilicities of anions are given in Table 6.5.

It was an important achievement in the field of ion transfer studies that the determination of lipophilicities of ions across the water|*n*-octanol interface became feasible with the help of the three-phase electrode approach [B 206, 269]. This is so important because the traditional measure of lipophilicity as a predictor of solute membrane partitioning is the partition coefficient in the *n*-octanol-water system ($\log P_{\mathrm{aq}}^{n-\mathrm{oct}}$). The lipophilic chain of *n*-octanol together with the hydrophilic hydroxyl group make *n*-octanol a good mimic for the major constituents of biological membranes (i.e., phospholipids). However, due to the non-polarizability of the water | *n*-octanol interface in the 4-electrode ITIES technique, no lipophilicity data of ions measured in that system were accessible until now. The non-polarizability of that interface is a result of not having yet found an appropriate lipophilic electrolyte for *n*-octanol to perform the necessary 4-electrode ITES measurements. Using the three-phase electrode approach the determination of standard Gibbs energies of ion transfer across the water | *n*-octanol interface is quite easy [B 206, 269].

The knowledge of the lipophilicities of amino acids and peptides [B 262, 266] is of essential importance to understand their biological activity, peptide interactions and peptide folding. Studying the transfer of mono anionic forms of various oligo peptides was performed to determine the individual contributions of the amino acid residues to the overall lipophilicity of the oligo peptides [B 266]. The effect of the *position* of an amino acid residue in the chain of a peptide is in some cases very pronounced, especially when an aromatic amino acid residue is placed next to the terminal amino acid at which the negative charge is located in the anionic form. Therefore, it is unreasonable to approximate the entire lipophilicity of peptide anions as additive functions of the contributions of their amino acid residues, as it has been proposed in all theoretical models for neutral peptides. A first study of the lipophilicities of various peptide anions and amino acid anions has been published [B 262, 266]. A part of the data is given here in Table 6.6.

Table 6.5. Formal potentials $E_c^{\ominus\prime}$, slope of the formal potentials vs. concentration of anions in aqueous phase, standard deviation of formal potentials, and standard Gibbs energies of ion transfer of some anions across the water|NB interface [B 259]

Anion	$E_c^{\ominus\prime}$ /mV	slope $E_c^{\ominus\prime}$ vs. log (c) / mV	$s(E_c^{\ominus\prime})$ /mV	$\Delta G^{\ominus}$ /kJ mol^{-1}
ClO_3^-	2	-55.3	6.43	25.40
BrO_3^-	60	-58.7	7.17	30.90
IO_3^-	74	-54.3	8.08	32.40
IO_4^-	-132	-56.4	2.00	12.50
OCN^-	45	-50.5	2.45	29.50
$SeCN^-$	-136	-43.0	5.30	11.80
CN^-	41	-58.1	4.43	29.60
N_3^-	14	-52.1	3.44	26.80
Monofluoroacetate	44	-54.4	5.48	29.90
Difluoroacetate	34	-48.5	3.90	28.90
Trifluoroacetate	-2	-60.1	1.79	25.30
Monochloroacetate	36	-51.5	4.73	29.10
Dichloroacetate	9	-58.0	1.15	26.40
Trichloroacetate	-66	-60.1	1.97	18.80
Monobromoacetate	12	-39.3	3.44	26.70
Dibromoacetate	-7	-59.0	2.00	24.80
Tribromoacetate	-94	-59.8	1.03	16.00
Monoiodoacetate	0	-54.6	1.20	25.10
Formiate	58	-56.4	2.40	30.60
Acetate	52	-58.0	1.50	30.10
Propionate	29	-54.6	0.80	27.98
Butyrate	11	-53.1	2.20	26.25
Valeriate	-31	-63.5	2.80	22.30
Capronate	-75	-60.3	1.40	18.10
Oenanthate	-115	-55.2	1.80	14.20
Caprylate	-125	-57.4	4.20	12.64
Pelargonate	-120	-52.9	3.20	13.40
Caprinate	-118	-58.4	2.50	13.60
Cyclopropane carboxylate	-20	-60.0	1.10	23.25
Cyclobutane carboxylate	-61	-57.8	1.40	19.30
Cyclopentan carboxylate	-100	-63.2	1.60	15.54
Cyclohexane carboxylate	-131	-56.8	2.80	12.54
Cycloheptane carboxylate	-155	-55.4	2.00	10.22

Table 6.6. The standard Gibbs energies of transfer, the standard potential of transfer, and the logarithm of the partition coefficients of monoanionic forms of amino acids and peptides as determined by three-phase electrode approach [B 266]

Peptide anions	$\Delta\varphi^{NB\ominus}_{aq,A^-}$ / V	$\Delta G^{NB\ominus}_{aq,A^-}$ / kJ mol^{-1}	$\log P^{NB\ominus}_{aq,A^-}$	slope $E_c^{\ominus'}$ vs. log[c] / mV
Trp$^-$	0.115	10.80	-1.90	-64
Trp-Ala$^-$	0.165	15.75	-2.75	-80
Trp-Gly$^-$	0.162	15.60	-2.73	-73
Trp-Val$^-$	0.120	11.60	-2.05	-75
Trp-Leu$^-$	0.100	9.50	-1.66	-73
Trp-Tyr$^-$	0.075	7.40	-1.30	-65
Trp-Phe$^-$	0.055	5.30	-0.93	-77
Trp-Trp$^-$	0.050	4.80	-0.85	-70
Trp-Gly-Gly$^-$	0.165	15.80	-2.75	-75
Trp-Gly-Tyr$^-$	0.165	15.00	-2.65	-74
Trp-Gly-GlyTyr$^-$	0.160	15.50	-2.70	-74
Leu-Leu$^-$	0.245	23.70	-4.15	-71
Leu-Leu-Ala$^-$	0.293	28.20	-4.95	-57
Leu-Leu-Gly$^-$	0.290	28.00	-4.91	-80
Leu-Leu-Leu$^-$	0.240	23.20	-4.05	-80
Leu-Leu-Tyr$^-$	0.205	19.70	-3.45	-56
Leu-Leu-Phe$^-$	0.180	17.50	-3.05	-64
Gly-Gly-Val$^-$	0.275	26.40	-4.60	-57
Gly-Gly-Leu$^-$	0.280	26.80	-4.70	-56
Gly-Gly-Phe$^-$	0.270	26.00	-4.55	-58
Gly-Trp-Gly$^-$	0.165	15.80	-2.75	-48
Gly-Gly-Trp$^-$	0.195	19.00	-3.35	-56
Lys-Tyr-Thr$^-$	0.310	30.00	-5.25	-58
Tyr-Ala-Gly$^-$	0.260	24.90	-4.40	-48

The Transfer of Chiral Ions Across the Water | Chiral Organic Liquid Interface

It has been shown that the transfer of ions from water to a *chiral* organic solvent can be studied with three-phase electrodes. Thus, it was possible to measure the differences in Gibbs energies of transfer for *chiral* ions from water to *chiral* liquids. By attaching a single droplet of a *chiral* liquid containing decamethylferrocene on a paraffin-impregnated graphite electrode and immersing that electrode in an aqueous solution containing *chiral* anions, the Gibbs energies of all four ion-solvent combinations can be determined (see Fig. 6.28).

For symmetry reasons it is expected that the Gibbs energies of transfer of a D-ion from water to the D-liquid is the same as that of the L-ion to the L-liquid. The same holds true for the combinations D-ion / L-liquid and L-ion / D-liquid. Square-wave voltammetric experiments conducted in aqueous solutions containing D- or L-anionic forms of some amino acids (phenylalanine, tyrosine, and lysine) performed with dmfc solutions in D- and L-2-octanol droplets allowed to determine these Gibbs energies of transfers relative to each other, i.e., the differences between $\Delta G_{D-ion}^{\theta,w\rightarrow D-liq}$ and $\Delta G_{D-ion}^{\theta,w\rightarrow L-liq}$, i.e. $\Delta\Delta G_{D-ion}^{\theta,w\rightarrow L-liq;D-liq}$, and between $\Delta G_{L-ion}^{\theta,w\rightarrow L-liq}$ and

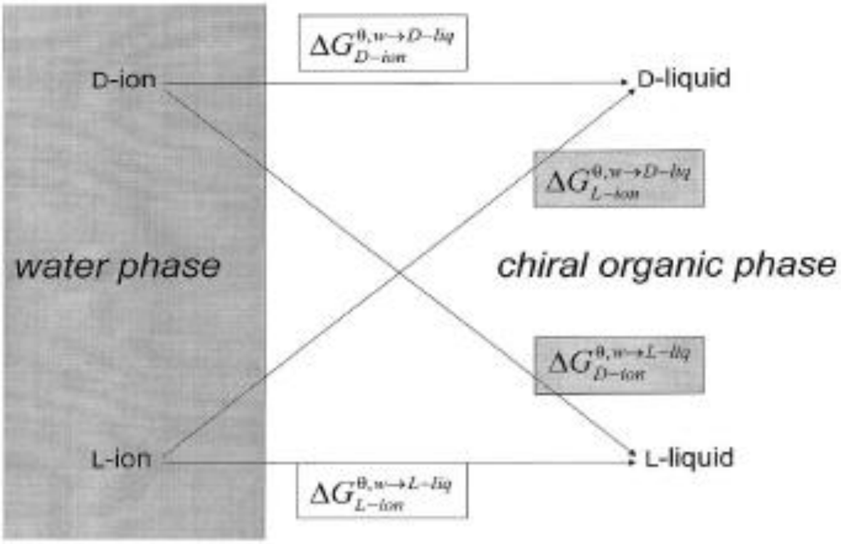

Fig. 6.28. Accessible Gibbs energies of transfer of D- and L-ions between water and a D- and L-liquid

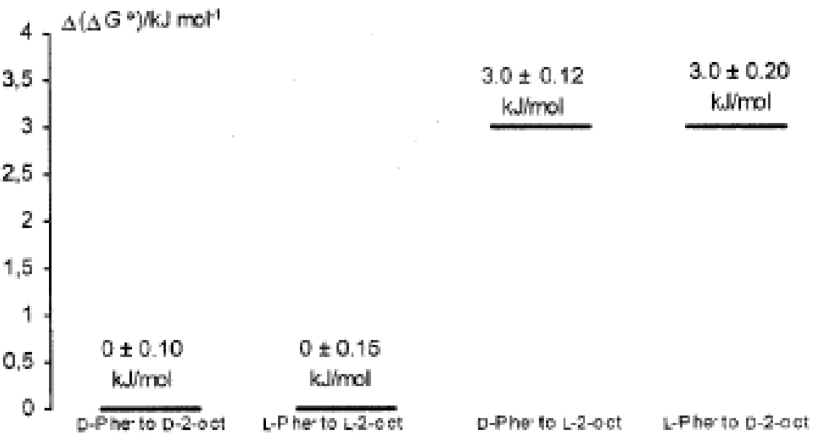

Fig. 6.29. Relations between the Gibbs energies of transfer of the anions of D- and L-phenylalanine from water to D- and L-2-octanol. The values for D-Phe- and L-Phe- have been set arbitrarily to zero. The values following the signs "±"denote to standard deviations

$\Delta G_{L-ion}^{\theta,w\to D-liq}$, i.e., $\Delta\Delta G_{L-ion}^{\theta,w\to L-liq;D-liq}$. In all studied combinations symmetrical solvation behavior has been observed, which is in complete agreement with theory. Thus, the energy of interactions between D-anions and D-2-octanol were identical with those between L-anions and L-2-octanol. The same holds true for the combinations D-anions and L-2-octanol and L-anions and D-2-octanol (see the example in Fig. 6.29). This figure illustrates that the three-phase electrodes with immobilized droplets allow a reproducible measurement of the rather small energetic differences caused by the chirality of solvents and dissolved ions, which have not yet been determined by other techniques.

When the transfer of D- and L-monoanionic forms of the amino acid tryptophan was followed across the water|D-menthol and water|L-menthol interface, asymmetrical solvation behavior was observed [B 221]. The reasons for this asymmetry may be adsorption or precipitation at the liquid|liquid interface, or even different kinetics.

6.2.2 The Determination of Standard Gibbs Energies of Transfer of Cations

Following the principles outlined for anion transfer with three-phase electrodes, the *reduction* of an electro-reducible compound dissolved in an organic liquid is required to transfer cations from water to an organic liquid. Figure 6.30 visualizes the electrode system. The reduction of Fe(III) tetra-

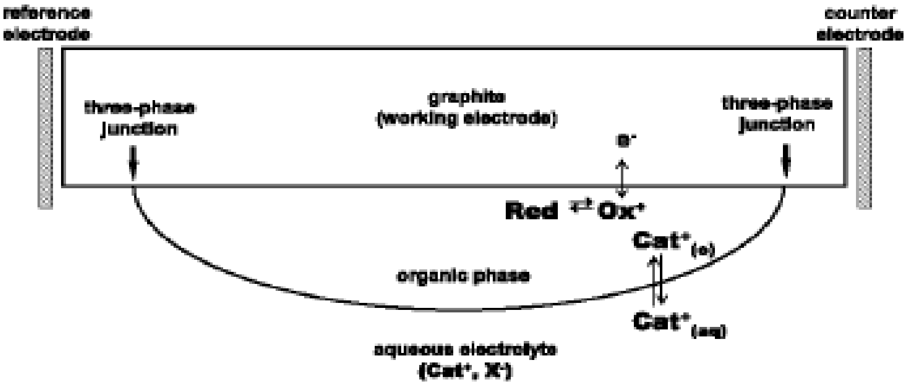

Fig. 6.30. Processes occurring at a three-phase electrode when an electroreducible compound is dissolved in the organic phase and cations are transferred across the interface water | organic liquid [B 271]

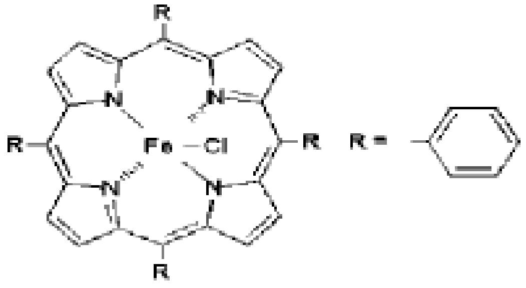

Fig. 6.31. Fe(III) tetraphenyl porphyrine chloride

phenyl porphyrine chloride [Fe(III)TPP-Cl] (Fig. 6.31) in a nitrobenzene microdroplet in a three-phase arrangement gives rise to well-developed square-wave voltammetric signals with a peak potential depending on the nature of the cations present in the aqueous phase [B 271]. The more lipophilic the cations in the aqueous phase are, i.e., the more *positive* the standard potentials of cation transfer from water to the organic liquid are, the easier is the reduction of [Fe(III)TPP-Cl]. As predicted by Eq. 6.15, this shifts the reduction to more positive potentials. Representative voltammograms showing the transfer of cations across the water|NB interface are shown in Fig. 6.32.

The standard Gibbs energies of transfer of several common inorganic cations as well as of some tetraalkyl ammonium cations across the water | NB interface have been determined using this approach. The data are given in Table 6.7.

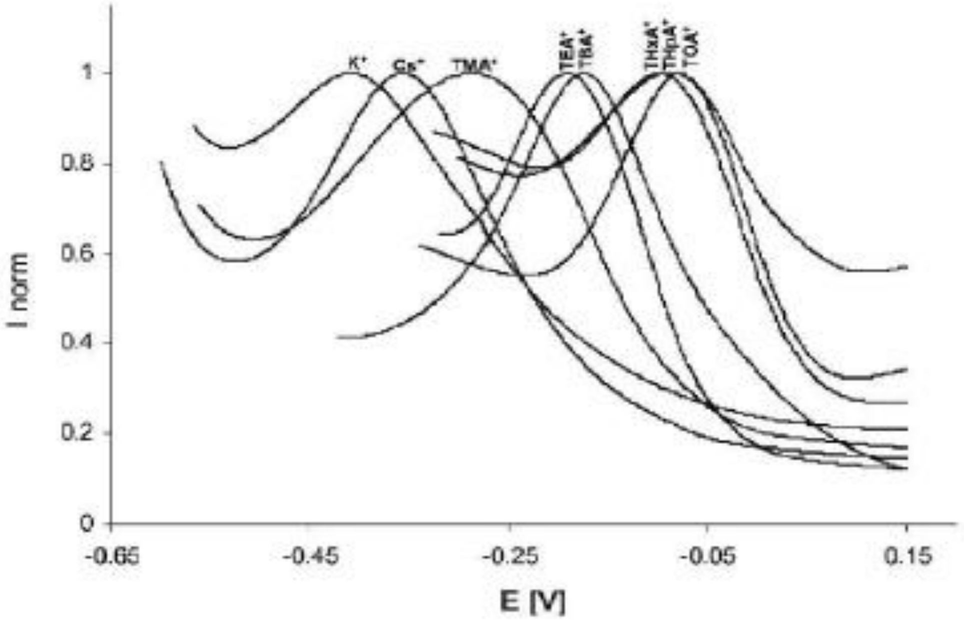

Fig. 6.32. Normalized square-wave voltammograms of the redox reaction of Fe(III)TPP-Cl in NB droplets accompanied by the transfer of cations from aqueous solution to NB [B 271]

Table 6.7. Standard Gibbs energies of transfer of cations across the water | NB interface determined from the formal potentials of the voltammograms of Fe(III)TPP-Cl at three-phase electrode [B 271]

Cations	$\Delta G^{NB^{\ominus}}_{aq,\,Cat^+}$ /k J mol^{-1}
K$^+$	22.65
Rb$^+$	19.80
Tl$^+$	19.30
Cs$^+$	17.80
TMA$^+$	9.60
TEA$^+$	-0.50
TBA$^+$	-8.20
THxA$^+$	-8.21
THpA$^+$	-8.78
TOA$^+$	-10.10

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