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Parallel Electrode Processes in Absence of Supporting Electrolyte. Further Strong Enhancement or Depression of Transport of Ionic Species*

by A. Nowicka[1], W. Hyk[1], Z. Stojek[1] and M. Ciszkowska[2]

[1]*Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warsaw, Poland*
E-mail: wojhyk@chem.uw.edu.pl; stojek@chem.uw.edu.pl
[2]*Department of Chemistry, Brooklyn College, CUNY, Brooklyn, NY 11210-2889, USA*
E-mail: MalgCisz@brooklyn.cuny.edu

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Several ferrocene derivatives, including 1,1′-ferrocenedimethanol, ferrocene, sodium ferrocenesulfonate, sodium ferroceneacetate and ferrocenylmethyltrimethylammonium hexafluorophosphate, were used to examine possible situations in voltammetry, if two of them are present together in the cell under the conditions of absence of supporting electrolyte.

The pairs of ferrocene derivatives were selected for the examination in such a way that one substrate was ionic and the other one neutral. Also, the diffusion coefficients of the species in the solution were sufficiently similar to avoid the effect of nonadditive voltammetric currents. If the ion formed from the neutral substrate and the second ionic substrate are the key ions in the process of preserving the electroneutrality in the diffusion layer at the electrode surface, a significant enhancement or depression of the transport of the ionic substrate takes place. The corresponding wave heights are either much higher (different signs of the ion charges) or lower (identical signs), compared to a situation, where the ionic substrate is present alone in a solution with no supporting electrolyte. The sequence of voltammetric waves of the two substrates determines, which wave is actually affected. The situations demonstrated in the paper may be useful in analytical strategies, aiming at enhancing or depressing a particular voltammetric signal.

Key words: voltammetry, migration, microelectrodes, electroactive counterion, ferrocene derivatives

Wide availability of microelectrodes made possible performing a variety of electrochemical experiments, including voltammetry, in the absence of supporting electrolyte [1,2,3,4]. This is because microelectrodes just reduce substantially possible ohmic potential drop in the cell. One of the consequences of removing-, or keeping at a low level, supporting electrolyte is that the transport of the species in a solution is of mixed diffusional and migrational nature, therefore, we can speak about, *e.g.*, migrational voltammetry. A measure of deficiency of supporting electrolyte is the so called support ratio, ξ, which is the ratio of concentrations of supporting electrolyte and analyte.

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

It is well known and was for the first time reported over 50 years ago [5], that under the conditions of low support ratio charged electroactive species give voltammetric waves of different height. The first rigorous theoretical models for this primary migrational effect, that either confirmed or questioned the related experimental findings and delivered new predictions, appeared in late eighties [6,7,8,9]. Regarding uncharged substrates, the heights of their voltammetric waves are virtually independent of supporting electrolyte concentration, however, an extra time and/or potential is needed to reach the steady state current under the conditions of low support ratio [10]. Several interesting physicochemical and analytical phenomena appear and are related to electrochemical measurements in the absence of supporting electrolyte. This has been covered in several review papers, *e.g.* [1,2,3,4].

The recent research activities in the area of mixed migrational and diffusional transport aim at perfecting both the analysis of the experimental data and the theoretical description of the currents. The conditions of using the principle of unchanging total concentration have been widened [11] and a convolutive approach to model voltammetry has been presented [12]. Also, unequal diffusion coefficients have been added to the model [13,14], natural [15] and forced convections [16,17] coupled to migration have been diagnosed, and a method of determination of diffusion coefficients of substrate and product for any support ratio has been worked out [18]. A rigorous theoretical treatment confirmed the validity of voltammetric theories, based on the electroneutrality assumption [19]. The migrational transport also appeared to have some importance in the electrochemistry of an arrangement of three phases [20,21,22,23].

In our view, not enough attention has been paid so far to the voltammetry of two or more substrates under the conditions of mixed diffusional and migrational transport (the secondary migrational effect appears). The literature experimental data are virtually limited to two very old polarographic papers, in which the reduction of an alkaline metal was reported to lead to an exaltation of the current in the presence of oxygen in the cell [24,25]. Using a simple model of the Nernst diffusion layer, Kharkats [26] was able to show theoretically, that the exaltation current was due only to migrational transport of the cations and the OH^- group. The same treatment failed to give a good agreement with experiment for the simultaneous reduction of two cations. Somewhat similar to the reduction of metal cation in the presence of oxygen is the problem of the metal dissolution and the simultaneous cation discharge from a binary electrolyte [27].

The aim of this paper is to illustrate experimentally other possible changes in migrational voltammograms, caused by the presence of two dissolved substrates in the system. The corresponding rigorous theoretical model is being developed. We want to demonstrate, what may happen to the voltammograms obtained in the absence of supporting electrolyte, if the ionic product of an electrode process of a neutral substrate meets, in the solution, a second substrate that is also ionic. Such situations may enhance substantially the migrational contribution to voltammetric waves of single substrates, no matter which red-ox couple is more or less positive.

The ferrocene derivatives were selected as objects in this investigation, due to their uncomplicated and reasonably fast electrode processes and comparable diffusion coefficients.

Somewhat related to this problem is that described by Abruña, Amatore, White and coworkers [28,29]. They demonstrated experimentally and digitally, that bimolecular electron transfer between members of the redox system that differ by +2 in oxidation state (*i.e.*, reproportionation) can strongly influence the magnitude of transport-limited currents, when ion migration contributes to the molecular transport. In our systems of two 1-e processes, the reproportionation reactions cannot take place. However, the migrational effects illustrated in this report might be affected by the red-ox equilibria in the way shown recently for diffusional transport by Leventis *et al.* [30]. They noted that for the oxidation reaction of two systems: Red1/Ox1 (less positive formal potential) and Red2/Ox2, at the potentials corresponding to the second plateau, Ox2 will oxidize Red1 in the solution. As a result, the concentration of Red1 will decrease in the diffusion layer and the concentration of Red2 will increase. In the presence of excess of supporting electrolyte, the total wave height will be affected up to 30% if Red1 and Red 2 differ substantially in the diffusion coefficients.

The systems selected for this work do not differ much in the diffusion coefficients, and additionally the depletion layer is spherical (microelectrodes are used). Therefore, at least under diffusional conditions, a substantial drop in the second wave should not take place. To find out, whether under the influence of electric field (migration), the above bulk equilibria have some influence on the transport, we have compared similar redox systems, which differ in the sequence of voltammetric waves, *i.e.* they have the wave potentials inverted.

EXPERIMENTAL

Voltammetric measurements were done using an AutoLab potentiostat controlled by a PC computer. A platinum disk microelectrode of 10.9 ± 0.2 μm in radius (nLab, Warsaw) served as the working electrode. Two platinum foils of the surface area 1 cm^2 were used as the counter and quasi-reference electrodes. The Pt quasi reference electrode was chosen to eliminate possible leaks of ions from the electrolytic bridge. Before each experiment the working electrode was initially polished with aluminum-oxide powders of various sizes (down to 0.05μm) on a wet pad (Buehler). Subsequently, before each voltammetric scan, the surface was renewed by brief polishing with 0.05 μm alumina. After each polishing, to remove alumina completely from the electrode surface, the electrode was rinsed with a direct stream of ultrapure water (Milli-Q, Millipore, conductivity of ~0.056 mS/cm). The electrode surface was also occasionally inspected optically with an Olympus, model PME 3, inverted metallurgical microscope. To minimize the electric noise, the electrochemical cell was kept in a grounded aluminum-foil Faraday cage.

The chemical compounds: ferrocene ($Fe(C_5H_5)_2$, 98%, abbreviation Fc) and 1,1′-ferrocenedimethanol ($Fe(C_5H_4)_2(CH_2OH)_2$, 98%, abbreviation Fc_($CH_2OH)_2$) were purchased from Aldrich. Sodium ferrocenesulfonate ($Fe(C_5H_5)\text{-}(C_5H_4)(SO_3^-)Na^+$, abbreviation Fc_$SO_3^-Na^+$), sodium ferroceneacetate ($Fe(C_5H_5)\text{-}(C_5H_4)(CH_2COO^-)Na^+$, abbreviation Fc_$CH_2COO^-Na^+$) and ferrocenylmethyltrimethylammonium hexafluorophosphate ($Fe(C_5H_5)\text{-}(C_5H_4)(CH_2N(CH_3)_3^+)PF_6^-$, abbreviation $FcTMA^+PF_6^-$) were synthesized in our laboratory according to the procedures available in the literature [31]. The above substrates were dissolved either in water (deionized water from the Milli-Q, Millipore system) or in acetonitrile (*p.a.*, Fluka). Lithium perchlorate ($LiClO_4$, 99%) and tetrabutylammonium perchlorate ($N\text{-}(C_4H_9)_4ClO_4$, 99%), both purchased from Fluka, were used as supporting electrolytes. Temperature was maintained at 22°C. The half-wave potentials of the voltammograms obtained in a given solution and measured *vs.* the Pt quasi reference electrode changed by 20–40 mV with additions of the second component, however, this did not affect the wave-height measurements.

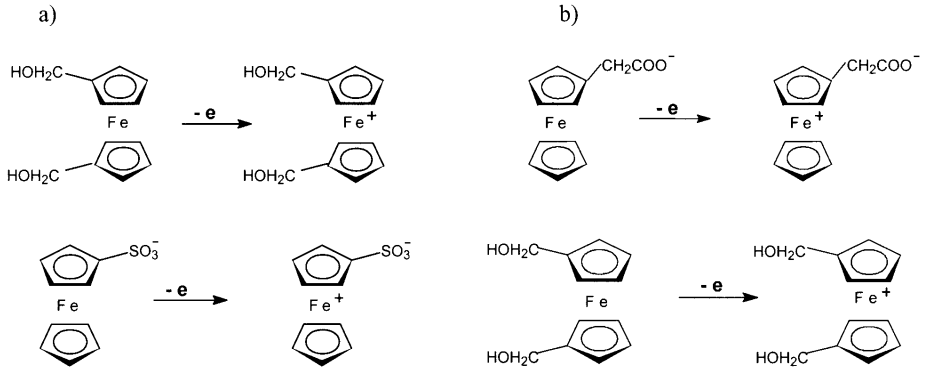
Two-component systems studied. Two electroactive compounds appropriately selected were added to the solutions to examine how their transport is affected in the absence of supporting electrolyte. The compounds of the mixtures do not differ in diffusion coefficient substantially. The basic electroanalytical characterization of the ferrocene derivative pairs is given in Table 1. The diffusion coefficients of all substrates and electrode-reaction products have been determined using the procedure published recently [18]. A comparison of the wave heights obtained for the compounds present alone and in the mixtures and for excess supporting electrolyte indicates that there is no substantial nonadditive effect [30]. The selection of the compounds and the preparation of the solutions were done in one of the following two ways. In the first way, one substrate was ionic and of a constant concentration (2 mM). This substrate was supposed to work as the counterion to the electrooxidation product of the second substrate. In the second way, the signs of the charges of one substrate and the electrooxidation product of the second substrate were the same. In consequence, the oxidation of the mixtures of two metallocene derivatives, if they are treated as one system, can be assigned to one of two groups of processes named below.

The first group is called by us the charge reversal group, since it delivers pairs of species for which the total initial charge is –1 and the total final charge is +1. In the first oxidation reaction of group I (see Scheme 1, a and b) the univalent cation is produced while the second substrate, which has a negative charge, works as its counterion (in the absence or deficiency of supporting electrolyte) and is responsible for maintaining the charge balance in the electrode vicinity. In other words, we can speak about specific migrational-electrostatic interactions, *i.e.* attractions, between the two ionic ferrocene-derivative species, which should enhance the transport rate of the anionic species to the microelectrode surface.

The second group is called by us the charge increase group, since it includes pairs of systems for which the total initial charge is +1 and the total final charge is +3. In the second group (see Scheme 2, a and b), the first component of the first two mixtures is oxidized to the univalent cation, and the second substrate (of charge +1) is oxidized to a +2 product. Since the product of the first electrode reaction and the second substrate have the same charge sign, the repulsion is expected to take place at the electrode surface in the absence of supporting electrolyte and the transport of the charged substrate to the electrode should be additionally slowed down.

Scheme 1

Charge reversal process ($z_{S,C} = -1$; $z_{P,C} = +1$; subscript c indicates cumulated charges)



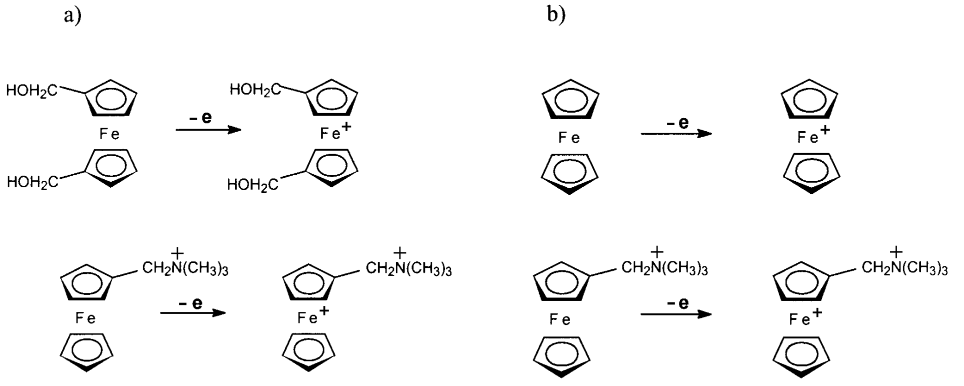
(solvent: water) (solvent: water)

Table 1. Voltammetric characteristics of the ferrocene derivatives used. D_S and D_P stand for the diffusion coefficients of the substrate and the product of the 1-e oxidation. The diffusion coefficients were determined using the procedure published in ref. [18]. K_{eq} denotes equilibrium for the electron exchange reaction between the product of the wave located at more positive potentials and the substrate of the less positive wave.

Mixture	Wave heights for the compounds present alone 2mM) / nA		Total wave height in the mixture (2mM:2mM) / nA	Difference between columns 3 and 4 / %	$D_S \pm s \times 10^9$ / m^2/s	$D_P \pm s \times 10^9$ / m^2/s	Solvent	K_{eq}
	individual	total						
Fc_(CH$_2$OH)$_2$	5.42				0.62 ± 0.02	0.59 ± 0.03		
and		9.74	9.86	1.3			H_2O / 0.1 M $LiClO_4$	1843
Fc_SO$_3^-$	4.32				0.58 ± 0.03	0.55 ± 0.04		
Fc_(CH$_2$OH)$_2$	5.42				0.62 ± 0.02	0.59 ± 0.03		
and		9.71	10.02	3.3			H_2O / 0.1 M $LiClO_4$	370
Fc_CH$_2$COO$^-$	4.29				0.51 ± 0.01	0.49 ± 0.02		
Fc	20.99				2.15 ± 0.05	2.06 ± 0.07		
and		30.88	30.30	1.9			CH_3CN / 0.1 M TBAP	6206
Fc_TMA$^+$	9.89				1.39 ± 0.03	1.45 ± 0.05		
Fc_(CH$_2$OH)$_2$	5.42				0.62 ± 0.02	0.59 ± 0.03		
and		8.96	9.18	2.3			H_2O / 0.1 M $LiClO_4$	692
Fc_TMA$^+$	3.54				0.42 ± 0.05	0.39 ± 0.04		

Scheme 2

Charge increase processes ($z_{S,C} = +1;\ z_{P,C} = +3$)



(solvent: water)

(solvent: acetonitrile)

RESULTS AND DISCUSSION

Pair Fc_SO_3^- Na^+ / Fc_$(CH_2OH)_2$ in water. The voltammetric behavior of the mixture consisting of Fc_SO_3^- Na^+ and Fc_$(CH_2OH)_2$ in the absence and presence of excess supporting electrolyte ($LiClO_4$) and for different concentration ratios is illustrated in Figure 1a. Both waves are very well defined. The wave of the methanol derivative of ferrocene is located at less positive potentials. The shift in the half wave potentials, which is a result of the use of Pt quasi reference electrode, is compensated by using the Fc_$(CH_2OH)_2$/ Fc_$(CH_2OH)_2^+$ scale. The slopes of the semi-logarithmic plots (excess supporting electrolyte) were determined as 57.6 and 58.6 mV, respectively, which means that the electrode processes were nearly reversible.

As it is seen in Figure 1a, the waves of uncharged Fc_$(CH_2OH)_2$, as expected, are independent of supporting electrolyte concentration. The second-wave height is higher by *circa* 1.6 times in the absence of supporting electrolyte when Fc_SO_3^- Na^+ is present alone. Formally, the ratio of wave heights of this compound in the presence and absence of supporting electrolyte should be 2 [7,8]. We attribute the smaller number obtained to incomplete neutralization of the primary acid and the presence of unwanted (impurities) ions (the sodium salt was prepared from the ferrocenesulfonic acid by treating it with sodium dissolved in ethanol; 5% deficiency of sodium *vs.* the amount of the acid was used). The second wave, in the absence of supporting electrolyte, increases strongly with additions of neutral Fc_$(CH_2OH)_2$ to the solution. This increase is illustrated in Figure 1b and reflects the enhanced transport of Fc_SO_3^- to the microelectrode to neutralize the cations produced within the first wave (Fc_$(CH_2OH)_2^+$). Under the conditions of Figure 1 the increase in the Fc_SO_3^- wave height, calculated *vs.* the wave height of Fc_SO_3^- alone in the absence of excess supporting electrolyte, reaches a factor of *circa* 2. This increase is purely due to the enhanced transport of Fc_SO_3^- triggered by the formation of the ferrocenedimethanol cation in the first reaction. It is worth noting here that the total increase in the wave height of $Fc\_SO_3^-$, calculated *vs*. the wave height of $Fc\_SO_3^-$ alone and in the presence of excess supporting electrolyte, is *circa* 3 times. We would expect a linear dependence in Figure 1b, however, the increase is apparently slower than linear. This may be caused again by the increased contribution of ionic impurities to the migrational transport of ions. The case presented in Figures 1a and 1b corresponds well to the classical reduction of metal cations in the presence of dissolved oxygen [24,25], where the OH^- ions formed from oxygen attracted metal cations to the electrode surface.

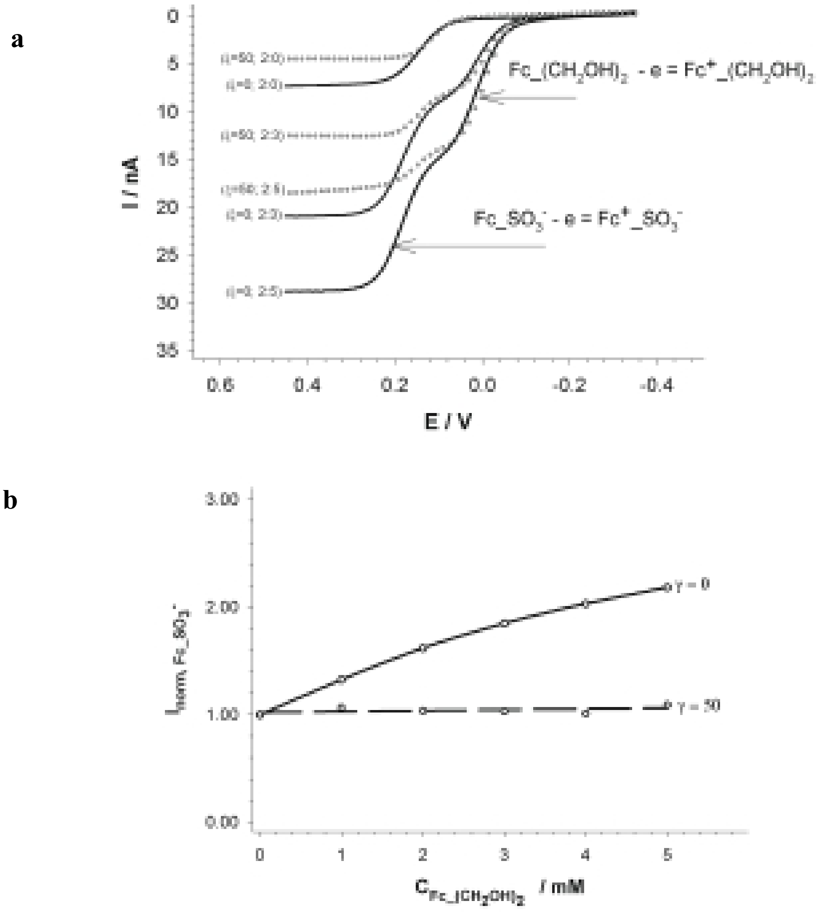


Figure 1. a) Experimental anodic voltammograms obtained in the absence ($\xi = 0$, solid line) and the presence ($\xi = 50$, dotted line) of excess supporting electrolyte. Mixture composition: sodium ferrocenesulfonate ($Fc\_SO_3^-Na^+$, constant concentration of 2 mM), and 1,1′-ferrocenedimethanol, ($Fc\_(CH_2OH)_2$, less positive potential). The values in parentheses show the support ratio and the molar ratio of the components in the mixture. Conditions: water, scan rate 10 mV/s, T = 22°C, supporting electrolyte: $LiClO_4$, Pt microelectrode of 10.9 μm in radius. E *vs*. $E_{Fc\_(CH_2OH)_2}$. b) Dependence of normalized ferrocenesulfonate current *vs*. concentration of added ferrocene dimethanol, for the absence and presence of supporting electrolyte. The currents are normalized vs. their initial values in the absence of ferrocenedimethanol.

Pair Fc_ $CH_2COO^-Na^+$ / Fc_$(CH_2OH)_2$ in water. Regarding just the charges of the species in the solution, this system is similar to the previous pair. However, now, the sequence of potentials of the waves of the anion and the neutral molecule is reversed. The ferroceneacetate anion is oxidized at less negative potentials compared to that of ferrocenedimethanol. The situation for the absence of supporting electrolyte is illustrated and compared with the excess supporting electrolyte case in Figure 2. An addition of neutral Fc_$(CH_2OH)_2$ to the solution does increase the Fc_ CH_2COO^- wave a little, however, a part of this increase is apparently caused by the overlapping

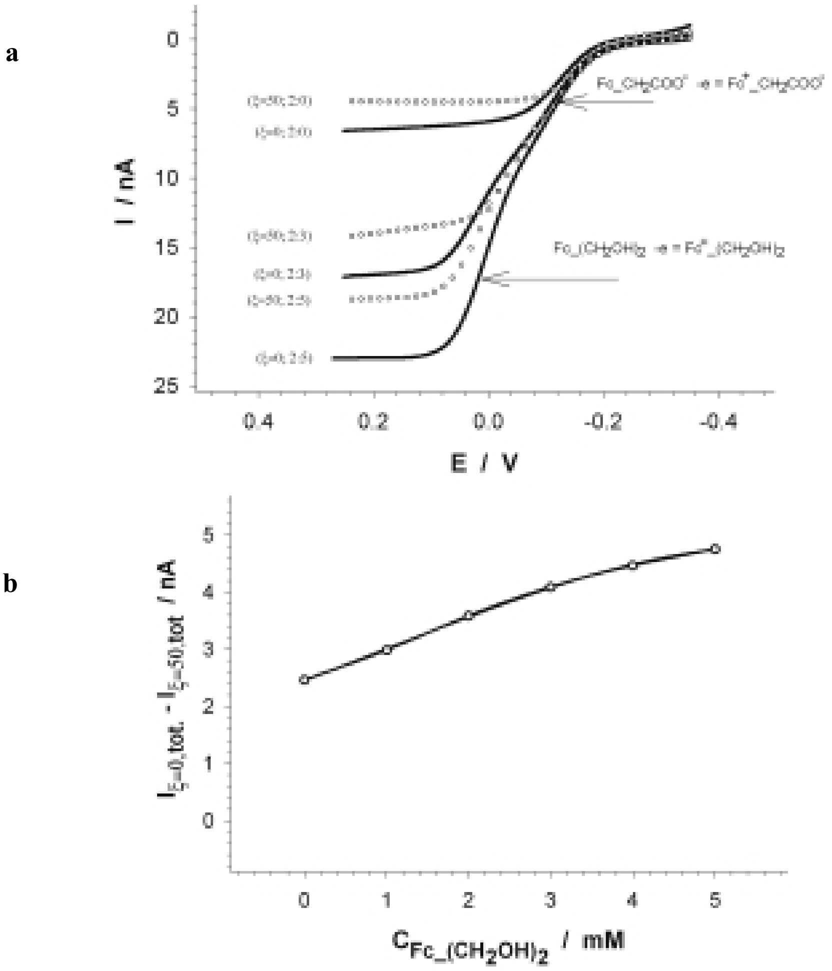


Figure 2. a) Experimental anodic voltammograms obtained in the absence ($\xi = 0$) of supporting electrolyte. Mixture composition: sodium ferroceneacetate (Fc_$CH_2COO^-Na^+$, constant concentration of 2 mM), and 1,1′-ferrocenedimethanol, (Fc_$(CH_2OH)_2$, more positive potential). The values in parentheses show the molar ratio of the components in the mixture. Conditions as in Figure 1.
b) Dependence of the difference between the total wave heights obtained in the absence of- and excess supporting electrolyte *vs*. concentration of added ferrocene dimethanol.

of both waves. Contrary to Figure 1, the heights of the waves of the neutral species (ferrocenedimethanol) are enhanced now *vs*. their values for the presence of excess supporting electrolyte. Clearly, this enhancement, as in the previous case, is also caused by the increased transport of the ferrocene-derivative anion to the microelectrode surface (where it is oxidized) to neutralize the charge of the ferrocenedimethanol cations produced. The effect obtained is illustrated quantitatively in Figure 2b, where the difference between the heights of total waves (at 0.45 V) obtained in the absence and presence of excess supporting electrolyte is plotted.

Pair $FcTMA^+PF_6^-$ / Fc in acetonitrile. Both the ferrocenylmethyltrimethylammonium cation and ferrocene are oxidized reversibly in acetonitrile in the presence of 0.1 M tetrabutylammonium perchlorate. The semi-logarithmic plots done for voltammograms of these compounds had the slopes of 59.1 and 58.2 mV, respectively. However, under linear potential scan conditions a fouling of the electrode surface has been noted. The wave plateaus were affected and the electrode needed polishing before each next scan. This fouling was apparently related to limited solubility of ferrocenylmethyltrimethylammonium dication. Therefore, we turned to normal pulse voltammetry (NPV). A pulse time of 100 ms was sufficiently short to keep the electrode repeatedly active over several scans. Typical NP voltammetric waves are shown, using the Fc/Fc+ potential scale, in Figure 3a under the conditions of increasing concentration of ferrocene. The wave height of ferrocenylmethyltrimethylammonium cation apparently strongly diminishes with increasing concentration of ferrocene; it drops by more than 50%, which is a lot compared with the drop of 15% [7,9] for the case of just absence of supporting electrolyte. This current drop is illustrated quantitatively in Figure 3b. The decrease in the $FcTMA^+$ wave height is caused by the fact that the ferrocene cation formed within the first wave attracts anions and repulses other cations (the electroneutrality must be preserved in the electrode proximity) and therefore the transport of $FcTMA^+$ to the microelectrode surface is slowed down.

Pair $FcTMA^+PF_6^-$ / Fc_$(CH_2OH)_2$ in water. This pair is in fact analogous to the previous pair. Uncharged ferrocene has been replaced by uncharged ferrocenedimethanol which is soluble in water and therefore the voltammetric examination could be done in aqueous media. The change in the wave height of ferrocenylmethyltrimethylammonium cation (the wave at more positive potentials) upon addition of ferrocenedimethanol is illustrated in Figure 4a. The normalized wave height is plotted *vs*. Fc_$(CH_2OH)_2$ concentration, for both the absence and presence of excess supporting electrolyte, in Figure 4b. Similarly to the previous case the drop in the $FcTMA^+$ wave height is caused by the fact that the ferrocenedimethanol cation formed within the first wave repulses other cations and therefore slows down the transport of $FcTMA^+$ to the microelectrode surface.

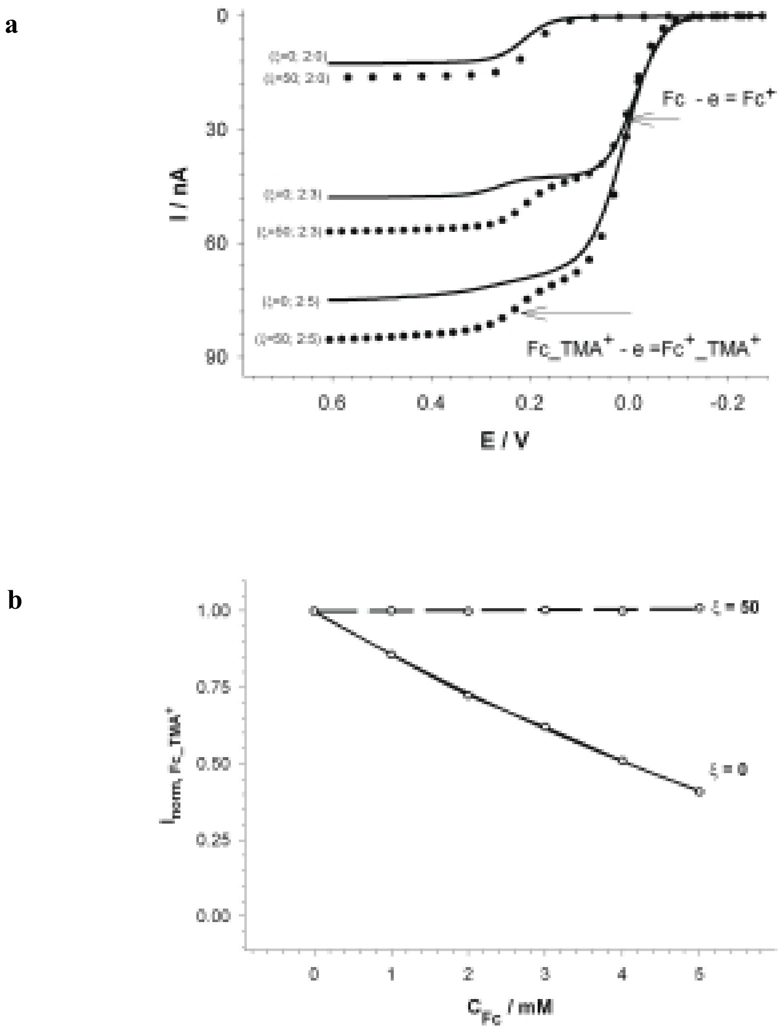


Figure 3. a) Experimental anodic NP voltammograms obtained in the absence (ξ = 0) of excess supporting electrolyte. Mixture composition: $FcTMA^+PF_6^-$ (constant concentration of 2 mM), and ferrocene (Fc, less positive potential). The values in parentheses show the support ratio and the molar ratio of the components in the mixture. Conditions: acetonitrile, pulse time: 100 ms, delay between pulses: 2 s, T = 22°C, supporting electrolyte: TBAP, Pt microelectrode of 10.9 μm in radius. E *vs.* E_{Fc/Fc^+}.

b) Dependence of normalized $FcTMA^+$ limiting current *vs*. concentration of added ferrocene, for the absence and presence of supporting electrolyte (0.1 M). The current is normalized *vs*. its initial value in the absence of ferrocene.

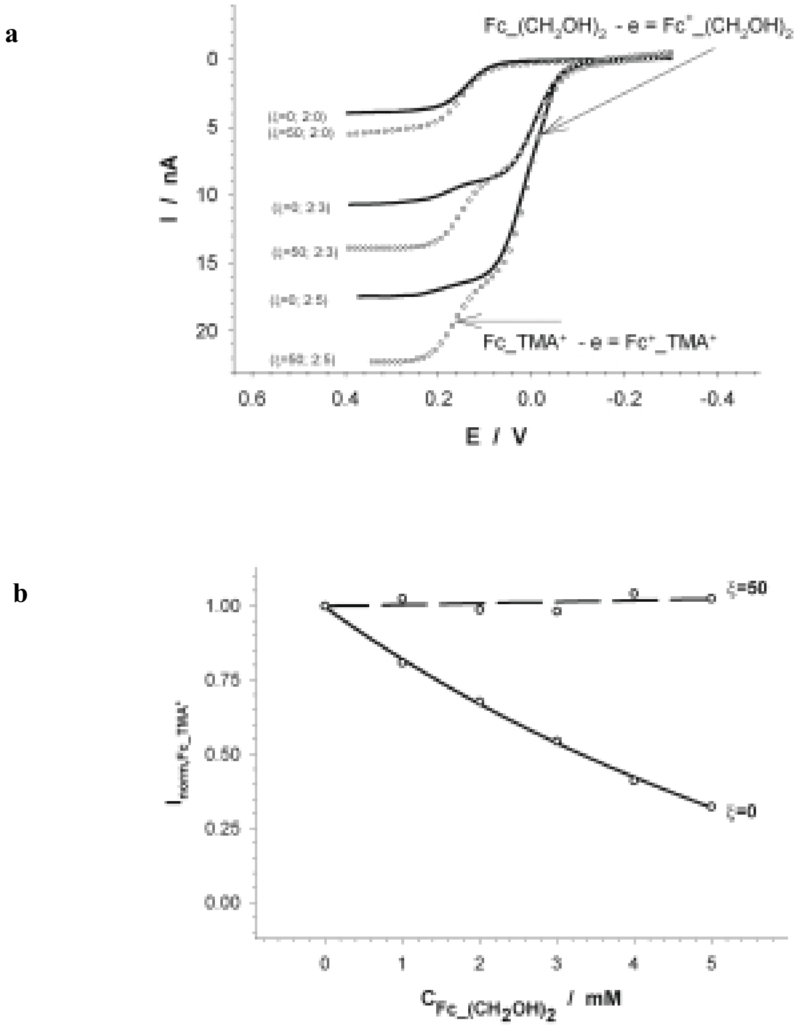


Figure 4. a) Experimental anodic voltammograms obtained in the absence (ξ = 0) of supporting electrolyte. Mixture composition: FcTMA$^+$PF$_6^-$ (constant concentration of 2 mM), and ferrocenedimethanol (Fc(CH$_2$OH)$_2$, less positive potential). The values in parentheses show the molar ratio of the components in the mixture. Conditions as in Figure 1.

b) Dependence of normalized FcTMA$^+$ current *vs.* concentration of added Fc(CH$_2$OH)$_2$, for the absence and presence (0.1 M) of supporting electrolyte. The current is normalized *vs.* its initial value in the absence of ferrocenedimethanol.

CONCLUSIONS

The experiments performed within this paper clearly demonstrate possible situations that may appear when two electroactive species, one ionic and the other neutral, are analysed voltammetrically in the absence of supporting electrolyte. We have selected anodic processes for the examination, however, the dependencies obtained should be identical for a pair of cathodic processes. The pairs of ferrocene derivatives were selected in such a way that both: the ion formed from the first substrate and the second ionic substrate are the key ions in the process of preserving the electroneutrality in the diffusion layer at the electrode surface.

The migrational effect can be easily predicted. If the two ions under consideration differ in charge, there is an extra enhancement of the transport of the second ionic substrate to the electrode surface. Interestingly, it is important which substrate is oxidized first. Depending on this, either the wave of the ionic substrate or the wave of the neutral substrate is enhanced. For the second group, where both ions are of the same sign, there should always be an extra depression of the transport of the second ionic substrate to the electrode surface. Here, the sequence of the two waves on the potential axis is important also and leads to a depression of the wave height of either the ionic or the neutral substrate. Only the situation for one sequence is presented. In fact, we have examined a system consisting of $FcTMA^+PF_6^-$ and ruthenocene, where ruthenocene is oxidized at more positive potentials, and found that the wave height of ruthenocene is depressed in the presence of $FcTMA^+PF_6$. However, because of low quality of the voltammograms obtained, we do not present the results here.

We believe the situations shown above may be used in analytical strategy to enhance or depress a particular voltammetric signal. A general theory (simulation) of the extra migrational contribution to the transport of ions in the case of parallel electrode processes under the conditions of absence of supporting electrolyte is being developed.

Acknowledgments

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