

# Steady-state voltammetric study of the reduction of decamethylferrocenium in dichloromethane at microelectrodes

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## Abstract

The reduction of decamethylferrocenium hexafluorophosphate in a low permittivity solvent, dichloromethane, was studied by steady-state voltammetry at microelectrodes, using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The limiting current was used to calculate the diffusion coefficient of the decamethylferrocenium cation and of its ion pair with the hexafluorophosphate anion at 298.15 K by employing a recent theory (OCSB [K.B. Oldham, T.J. Cardwell, J.H. Santos, A.M. Bond, J. Electroanal. Chem. 430 (1997) 25]) which takes into account the effect of ion association on the limiting currents. The OCSB theory describes accurately the contribution of migrational processes to the overall Faradaic current when variable quantities of supporting electrolyte are added to the solution. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Decamethylferrocenium hexafluorophosphate; Tetrabutylammonium hexafluorophosphate; Microelectrodes; Steady-state voltammetry; Ion association; OCSB theory

## 1. Introduction

Among the many advantages of the use of microelectrodes is the possibility of performing voltammetric studies in highly resistive media such as benzene [1], gases [2], ice [3] and supercritical fluids [4–6], where electrodes of conventional size are affected by an extensive *IR* drop.

Microelectrodes have been successfully employed in voltammetric investigations in organic solvents even in the absence of supporting electrolyte. Studies of the oxidation of ferrocene in acetonitrile and toluene [7] have shown that as the solvent polarity diminishes, the large *IR* drop makes the potential analysis extremely difficult in terms of wave shifting, but steady state currents may be obtained and reliable limiting current data can be inspected.

The use of an excess of supporting electrolyte to decrease the ohmic effect in these systems helps to obtain true diffusional limiting currents, but does not avoid the problem of assigning the diffusion coefficient to the real species in solution. This is due to the high ion-pair formation tendency of the support electrolyte and also to ion-pair formation between the electroactive ion and the supporting counterion. Usually it is not clear in these systems which fraction of the limiting current could be attributed to the free electroactive ion.

In this work we undertook the study of the limiting current for the reduction of decamethylferrocenium in dichloromethane (dielectric constant 8.93 at 298.15 K) at a platinum microdisc using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Both the electroactive and the supporting electrolytes are highly associated in this solvent [8] and the effect of the migrational and diffusional contributions could be varied by changing the ratio of supporting to electroactive electrolyte concentration.

The  $\text{Fe}(\text{Cp}^*)_2^{+/0}$  couple studied in this work has been proposed previously as an internal redox standard for studying solvent effects on the thermodynamics of electron transfer of other couples [9]. The arguments used

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to address the advantage of replacing the well known  $\text{Fe}(\text{Cp})_2^{+/0}$  couple by  $\text{Fe}(\text{Cp}^*)_2^{+/0}$  are based on a larger radius/charge ratio and minimal geometric change of the ligands as a result of an electron transfer. It has been shown that minimal geometric change of the ligands should occur as a consequence of the redox state.  $\text{Fe}(\text{Cp}^*)_2^+$  and  $\text{Fe}(\text{Cp}^*)_2$  have essentially the same molecular structure in the solid state [10] and presumably in solution.

Also, an accessible formal redox potential ( $E_f$ ) in a wider variety of solvents and higher stability of both redox states in the presence of molecular oxygen (the  $\text{Fe}(\text{Cp})_2^+$  ion decomposes readily in the presence of aerial oxygen [11]) makes the  $\text{Fe}(\text{Cp}^*)_2^{+/0}$  redox couple more attractive as a reference redox standard and is superior in most respects to the  $\text{Fe}(\text{Cp})_2^{+/0}$  couple.

The aim of this work is to analyze the effect of ion pairing on the limiting currents at microelectrodes, employing theoretical models to determine the diffusion coefficients of the free decamethylferrocenium ion and its ion-pair with hexafluorophosphate. This is the first step in a more comprehensive study devoted to the use of microelectrode voltammetry in the study of transport processes in supercritical systems.

## 2. Theory

### 2.1. Effect of supporting electrolyte on the limiting current

Amatore et al. [12] solved the mass transport equations for cylindrical electrodes in media of low ionic strength, taking into account migrational effects and the variation of the diffusion coefficients with the amount of supporting electrolyte added for the cases of the oxidation of ferrocene and the reduction of the cobaltocenium ion in acetonitrile.

Oldham [13] developed a simple model to predict the effect of the supporting electrolyte concentration on the general pattern of the steady-state current–potential curves. The theory describes the combined effect of diffusion and migration on the shape of steady state voltammetric waves under variable quantities of supporting electrolyte for singly charged and uncharged species.

Aoki [14] solved the model for a microsphere of radius  $r_s$ , leading to the following expression for the limiting current,  $I_L$ :

$$I_L = 2\pi F D r_s \{2(c_E + c_S) - 2[c_S(c_E + c_S)]^{1/2}\} \quad (1)$$

where  $c_S$  and  $c_E$  are the concentration of supporting and electroactive electrolytes, respectively,  $D$  is the diffusion coefficient of the electroactive species and  $F$  is the Faraday constant. For a microdisc of radius  $r$  the former expression is valid if we multiply by a factor  $2/\pi$  [15].

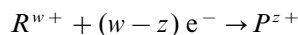
Cooper and Bond [16] tested the theory for the reduction of cobaltocenium in dichloromethane and acetonitrile, using tetrabutylammonium perchlorate as supporting electrolyte. They varied the support ratio, defined as:

$$\text{SR} = \frac{c_S}{c_E} \quad (2)$$

They found that for  $\text{SR} < 1$  there is a rapid increment of the measured limiting current, with a slight decrease for  $\text{SR} \ll 1$ . Also, it was found that the limiting current in the absence of supporting electrolyte ( $\text{SR} = 0$ ) doubled the diffusional limiting current in excess of supporting electrolyte ( $\text{SR} = \infty$ ) such as predicted by Eq. (1).

While the agreement between experimental results and theory was good in the case of measurements in dichloromethane, the measured migrational current in acetonitrile was underestimated by the theory. The reason for such behavior is not understood well and it was ascribed to differences in the transport numbers of the tetrabutylammonium and cobaltocenium cations, or to an ionic strength effect not well understood.

Cooper and Bond [17] extended the theory to redox processes involving more than one electron, between species of the same charge, including neutral species:



The results are expressed in terms of the ratio between the limiting current in absence of supporting electrolyte,  $I_L$ , and the pure diffusional limiting current in excess of supporting electrolyte,  $I_d$ :

$$\frac{I_L}{I_d} = (w + 1) \left[ 1 + \frac{wz}{(w - z)} \ln \left( \frac{z(w + 1)}{w(z + 1)} \right) \right] \quad (3)$$

This approach allowed any number of electrons to be transferred without restrictions on the ion charge for both reactants and products. The theory departed from the experimental evidence in the cases where the half-wave potential was far away from the potential of zero charge, and the reason for this failure was ascribed to the effect of a electroneutrality breakdown on the double layer.

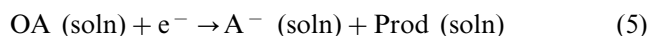
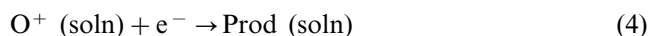
None of these approaches considered the possibility of ion association, even when it is well known by analysis of the electrical conductivity of electrolytes, that strong ion pair formation is expected in solvents of low permittivity.

### 2.2. The OCSB theory

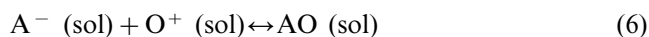
The effect of ionic association on the limiting voltammetric currents on microelectrodes has been considered only recently by Oldham, Cardwell, Santos and Bond (OCSB) [18], who included the formation of ion pairs in electrochemical processes on hemispheric microelec-

trodes through the ion association constant of both the electroactive species and supporting electrolyte. Furthermore, the possibility of including neutral and ionic species with distinct diffusion coefficients was also allowed. We briefly summarize in this Section the main features of the OCSB model.

The theory is applicable to any steady-state one-electron process:



OA being the ion pair formed between the electroactive cation  $\text{O}^+$  and the anion  $\text{A}^-$ , through the equilibrium:

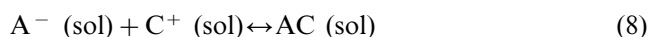


characterized by the equilibrium quotient:

$$\beta_2 = \frac{c_2}{c_1 c_3} \quad (7)$$

where the identity, charge and contribution to the limiting current of the different species can be found in Table 1. Because the ion-pair/free ion equilibrium is assumed to take place instantaneously at all points in the system, we could consider the ion-pair as an electroactive specie even when the cation  $\text{O}^+$  is the only electroactive species.

The theory also consider the ion association of the supporting electrolyte AC:



with

$$\beta_4 = \frac{c_4}{c_3 c_5} \quad (9)$$

The concentrations of the five species could be obtained from Eqs. (7) and (9) and the material balances:

$$c_1^b + c_2^b = c_E \quad (10)$$

$$c_4^b + c_5^b = c_S \quad (11)$$

$$c_2^b + c_3^b + c_4^b = c_S + c_E \quad (12)$$

where  $c_E$  and  $c_S$  represent the analytical concentrations of the salt that contains the electroactive species and the supporting electrolyte, respectively.

Table 1  
Species considered in the example above for the reduction of a singly charged electroactive cation

Species	Role	$i$	$z_i$	$v_i$
$\text{O}^+$	Electroactive cation	1	1	$1-f$
AO	Electroactive ion pair	2	0	$f$
$\text{A}^-$	Anion (common)	3	-1	$-f$
AC	Supporting ion pair	4	0	0
$\text{C}^+$	Supporting cation	5	1	0

The conservation equation for a hemispherical electrode of radius  $r_s$  is given by:

$$0 = \frac{v_i I_L}{F} + G_i + 2\pi r^2 D_i \left[ \frac{\partial c_i}{\partial r} + z_i c_i \left( \frac{F}{RT} \right) \left( \frac{\partial \phi}{\partial r} \right) \right] \quad (13)$$

where the first term represents the creation (or depletion) of the species  $i$  for the electrode reaction,  $G_i$  is the rate of generation of the species  $i$  by ion association or dissociation and the third term combines the concentration change by diffusion and migration at a radial distance  $r$  from the electrode ( $\phi$  is the local electrical potential).

These conservation equations for each species, along with the boundary conditions on the electrode surface:

$$c_1^s = c_2^s = 0 \quad (14)$$

and

$$c_3^s = c_5^s \quad (15)$$

have no analytical solution, but it is possible to find a numerical algorithm to calculate  $I_L$  in terms of the analytical concentrations  $c_E$  and  $c_S$ ,  $\beta_2$ ,  $\beta_4$  and the five diffusion coefficients,  $D_i$ .

Defining the variable  $x = (r - r_s)/r$ , and after some algebra:

$$\frac{I_L}{4\pi r_s F D_1} = \frac{D_2 c_2^b}{D_{13}} + c_3^b - c_5^s + \frac{D_4 (c_4^b - c_5^s)}{D_{35}} \quad (16)$$

where  $1/D_{13} = (1/D_1 + 1/D_3)/2$ , with a similar definition for  $D_{35}$ .

The concentrations in the bulk ( $c_i^b$ ) are known, but one must know the concentrations on the electrode surfaces,  $c_3^s$  and  $c_4^s$ . New variables are defined:

$$t = \frac{D_2 \beta_2 c_E}{D_{13}} \quad (17)$$

$$u = \frac{D_2 \beta_2 c_E}{D_3} \quad (18)$$

$$v = \frac{D_4 \beta_4 c_E}{D_{35}} \quad (19)$$

$$y_i = \frac{c_i}{\beta_i c_E^2} \quad (20)$$

that allows Eq. (16) to be written as:

$$\frac{I_L}{4\pi r_s F D_1 c_E} = t y_2^b + (y_2^b + y_4^b)^{1/2} + (y_4^b)^{1/2} - v (y_4^b - y_5^b) \quad (21)$$

where:

$$y_2^b = \frac{c_3^b}{[c_E (1 + \beta_2 c_3^b)]} \quad (22)$$

and

$$y_4^b = \frac{c_5 c_3^b}{[c_E^2 (1 + \beta_4 c_3^b)]} \quad (23)$$

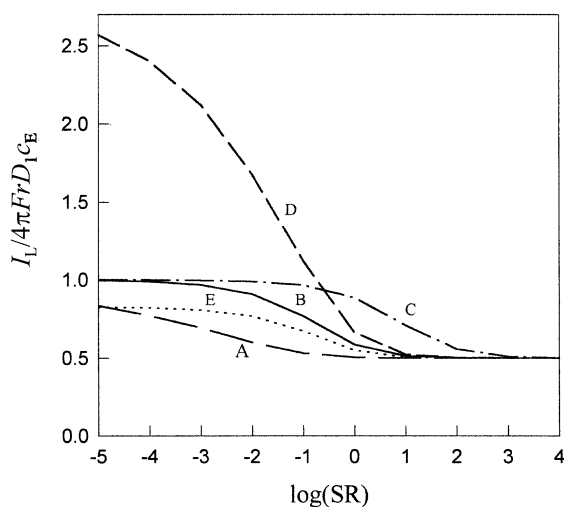


Fig. 1. Limiting currents as a function of the support ratio. Curves A–C correspond to situations where all the diffusion coefficients are equal. (A)  $\beta_2c_E = 100$ ,  $\beta_4c_E = 1$ ; (B)  $\beta_2c_E = 1$ ,  $\beta_4c_E = 1$ ; (C)  $\beta_2c_E = 1$ ,  $\beta_4c_E = 100$ . Curves D and E correspond to cases where  $\beta_2c_E = 1$ ,  $\beta_4c_E = 1$  with  $D_3/D_1 = 0.1$  (curve D) and  $D_3/D_1 = 10$  (curve E) with all other  $D_i = D_1$ .

$y_4^s$  is obtained by means of a numerical algorithm [18]. Thus, it is possible to calculate the limiting current for any practical condition if  $\beta_2c_E$ ,  $\beta_4c_E$ ,  $c_S/c_E$  and the four diffusion coefficients ratios,  $D_i/D_1$  ( $i = 2, 3, 4, 5$ ) are known.

Fig. 1 illustrates the limiting current as a function of SR for different values of  $\beta_2$  and  $\beta_4$  and different values of the diffusion coefficients. It can be noted that in the case where all the diffusion coefficients are equal and  $\beta_2 \leq \beta_4$ , the limiting current in the absence of the supporting electrolyte ( $SR \rightarrow 0$ ) is twice the value in excess of the supporting electrolyte ( $SR \rightarrow \infty$ ). The concentration of the supporting electrolyte needed to eliminate the migrational component is lower when this electrolyte is less associated as compared to the association of the electroactive electrolyte (compare curves A and C).

Curves D and E show how an increase in the ratio between the diffusion coefficient of the supporting electrolyte and the electroactive electrolyte influence the limiting current in the case of a low concentration of supporting electrolyte.

For several particular cases [18] the limiting current can be obtained explicitly. The results summarized below correspond to a microdisc of radius  $r$ , the geometry used in this work, under the following conditions:

(a) No supporting electrolyte ( $c_S = 0$ )

$$\frac{I_L}{8FrD_1c_E} = \frac{D_2}{D_3} + \left(1 - \frac{D_2}{D_3}\right) \frac{(1 + 4\beta_2c_E)^{1/2}}{2\beta_2c_E} \quad (24)$$

In this case the limiting current depends on the diffusivities of the three electroactive species and the ion pair formation constant. For the case of strong association ( $\beta_2c_E > 100$ ), Eq. (24) becomes:

$$I_L = 8FD_2 \left( \frac{1}{2} + \frac{D_1}{2D_3} \right) c_E r \quad (25)$$

and the limiting current is determined mainly by the ion pair. For weak association ( $\beta_2c_E < 1$ ):

$$I_L = 8FD_1c_E r \quad (26)$$

the limiting current is dominated by the electroactive cation.

(b) Overwhelming support ( $c_S \gg c_E$ )

The electroactive ions are paired and transport is diffusive

$$I_L = 4FD_2c_E r \quad (27)$$

The greater  $\beta_2$  is, the lower the concentration  $c_S$  is needed to reach this limit. It should be emphasized that Eq. (27) relates the limiting current to the diffusivity of the ion pair.

The only experimental test available for the OCSB theory has been conducted by the authors themselves [19]. They evaluated the reduction and oxidation of uncharged copper diethyldithiocarbamate, the reduction of silver cations and the oxidation of bromide anions in toluene at various concentrations of electroactive species and supporting electrolyte (tetrahexylammonium hexafluorophosphate). However, the range of support ratios that was studied successfully was restricted by the solubility of the supporting electrolyte and the severe ohmic polarization encountered when the ionic content was low. In addition, the association constants  $\beta_i$  and all the diffusion coefficients  $D_i$  for the different species in toluene had to be estimated crudely by matching the sigmoidal shape of the  $I_L$  versus log SR plot with the experimental data, and the values guessed probably do not represent a unique set due to the multiplicity of fitting parameters.

The aim of this work is to provide a further demonstration of the utility of the OCSB theory by carrying out electrical conductivity and steady state voltammetry experiments in low dielectric constant media for a given pair of electroactive and supporting salts.

### 3. Experimental

Dichloromethane ( $\text{CH}_2\text{Cl}_2$  Baker, HPLC grade) and 1,2 dichloroethane (Aldrich, >99%) were distilled prior to use. Acetonitrile (MeCN, Baker, HPLC grade) and acetone (Aldrich, >99.9%) were used without further purification.

Ferrocene (BDH) and tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , Fluka, electrochemical grade) were used as received. Decamethylferrocenium hexafluorophosphate ( $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ , with  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) was synthesized and purified following a literature procedure [20]. All solids were stored in a vacuum desiccator.

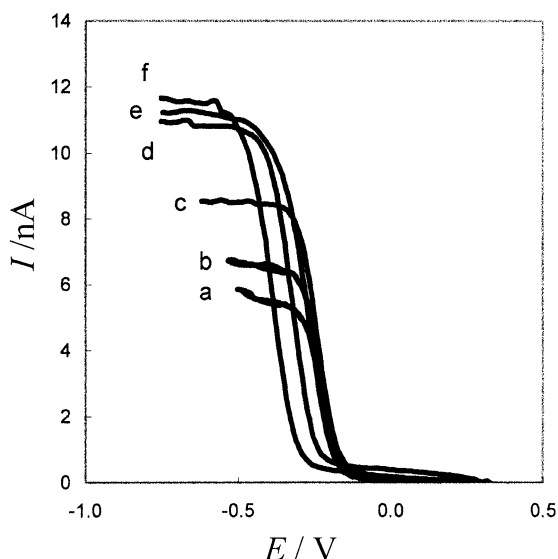


Fig. 2. Polarization curves for the reduction of  $10^{-3}$  M  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  at 298.2 K with variable concentrations of  $\text{Bu}_4\text{NPF}_6$ : (a)  $1.03 \times 10^{-1}$ ; (b)  $1.06 \times 10^{-2}$ ; (c)  $1.61 \times 10^{-3}$ ; (d)  $1.22 \times 10^{-4}$ ; (e)  $1.22 \times 10^{-5}$ ; (f)  $1.22 \times 10^{-6}$  mol  $\text{dm}^{-3}$ . Potentials vs. a Ag pseudo reference electrode.

Electrochemical experiments were made with a nominal 25  $\mu\text{m}$  diameter Pt microelectrode as a working electrode, fabricated by sealing a Pt wire in a glass tube (6 mm o.d., 1 mm i.d.) and exposing the Pt wire by polishing the glass on a soft cloth first with emery paper and followed by alumina (9, 3 and 0.05  $\mu\text{m}$  mesh). Traces of polishing material were eliminated by immersing the tip of the electrode in an ultrasonic bath for 15 min, after which the electrode was rinsed with water, acetone, and left to dry. A silver wire soldered to the Pt microwire acted as an external contact.

The microelectrode diameter was determined by measuring the limiting current of a standard solution of  $1.10 \times 10^{-4}$  mol  $\text{dm}^{-3}$  ferrocene in acetonitrile, using  $0.01$  mol  $\text{dm}^{-3}$   $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte. From Eq. (27) for the limiting current of a microdisc, along with the diffusion coefficient for ferrocene in acetonitrile ( $D = 2.35 \times 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ ) [21] an effective diameter of  $24.9 \pm 0.2$   $\mu\text{m}$  was obtained for the platinum microelectrode.

Table 2  
Limiting current for the reduction of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  on a platinum microdisc in  $\text{CH}_2\text{Cl}_2$  at 298.15 K at several concentrations of supporting electrolyte

$c_s/\text{mol dm}^{-3}$	$c_E/\text{mol dm}^{-3}$	SR	$I_L/\text{nA}$	$I_L^{\text{norm}}/\text{nA mol dm}^{-3}$	$I^*$ experim.	$I^*$ OCSB
$1.02 \times 10^{-1}$	$1.01 \times 10^{-4}$	$1.01 \times 10^3$	0.52	$5.15 \times 10^3$	1.00	1.00
$1.03 \times 10^{-1}$	$1.00 \times 10^{-3}$	$1.03 \times 10^2$	5.50	$5.58 \times 10^3$	1.08	1.02
$1.06 \times 10^{-2}$	$1.06 \times 10^{-3}$	$1.00 \times 10^1$	6.50	$6.13 \times 10^3$	1.19	1.22
$1.61 \times 10^{-3}$	$1.11 \times 10^{-3}$	$1.45 \times 10^0$	8.50	$7.65 \times 10^3$	1.49	1.58
$1.22 \times 10^{-4}$	$9.86 \times 10^{-4}$	$1.23 \times 10^{-1}$	10.0	$1.01 \times 10^4$	1.85	1.97
$1.22 \times 10^{-5}$	$9.70 \times 10^{-4}$	$1.25 \times 10^{-2}$	10.8	$1.11 \times 10^4$	1.96	2.07
$1.22 \times 10^{-6}$	$9.78 \times 10^{-4}$	$1.24 \times 10^{-3}$	11.0	$1.12 \times 10^4$	2.17	2.14

A Pt wire, 1 mm in diameter, served as the counter electrode while a silver wire (1 mm in diameter) acted as a pseudo-reference electrode.

The solvent chosen for electrochemical measurements was  $\text{CH}_2\text{Cl}_2$  since all the solids were fairly soluble at 298 K. Due to the high volatility of  $\text{CH}_2\text{Cl}_2$ , prior to the preparation of stock solutions dry  $\text{N}_2$  was bubbled to eliminate  $\text{O}_2$  content. No other gas was passed through  $\text{CH}_2\text{Cl}_2$  during the subsequent experiments to minimize evaporation and narrow-necked flasks (20  $\text{cm}^3$ ) were always employed.

Cyclic voltammetry was performed at  $10 \text{ mV s}^{-1}$ , in a compromise to keep the solvent loss to a minimum and maintain steady state currents. Electrochemical data were recorded using a potentiostat (Oxford Instruments) provided with a picoammeter and connected to a PC through an IEEE-488 acquisition card.

#### 4. Results and discussion

Solutions of the electroactive salt  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  ( $\sim 10^{-3}$  mol  $\text{dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$  containing variable quantities of supporting electrolyte  $\text{Bu}_4\text{NPF}_6$  were prepared, so that different support ratios (SR) could be studied.

Cyclic voltammeteries for the reduction of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  were performed for each SR at least three times, with a reproducibility of  $\pm 3\%$ . The voltammetric curves (negative scan only) are displayed in Fig. 2.

In order to compare the limiting currents measured at different concentrations of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ , we defined a normalized limiting currents,  $I_L^{\text{norm}}$ :

$$I_L^{\text{norm}} = \frac{I_L}{c_E} \quad (28)$$

and a reduced limiting current,  $I^*$ :

$$I^* = \frac{I_L^{\text{norm}}(\text{SR})}{I_L^{\text{norm}}(\text{SR} \rightarrow \infty)} \quad (29)$$

The mean limiting currents measured for different values of SR are reported in Table 2, along with the corresponding normalized and reduced limiting currents.

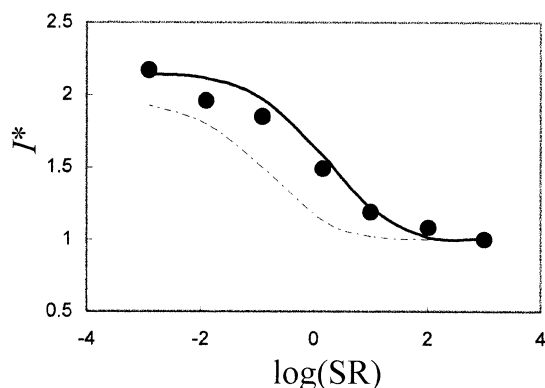


Fig. 3. Comparison of the OCSB theory (solid line) and equation (1) (dashed line) against experimental data (black dots) reported in Table 2 for the reduction of decamethylferrocenium hexafluorophosphate in  $\text{CH}_2\text{Cl}_2$  at 298.15 K using variable quantities of tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Table 3  
Diffusion coefficients of the  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  species in  $\text{CH}_2\text{Cl}_2$  at 298.15 K

Species	$10^5 D_i/\text{cm}^2 \text{ s}^{-1}$ (OCSB)	$10^5 D_i/\text{cm}^2 \text{ s}^{-1}$ (NE)
$\text{Fe}(\text{Cp}^*)_2^+$	1.63	1.35
$\text{PF}_6^-$	2.88	2.39
$(\text{Fe}(\text{Cp}^*)_2^+, \text{PF}_6^-)$	1.07	0.84

The equilibrium quotients  $\beta_2$  and  $\beta_4$  for the ion pair formation reactions (6) and (8) have been obtained from electrical conductivity measurements in  $\text{CH}_2\text{Cl}_2$  at 298.15 K [22] and the values are  $3.50 \times 10^3$  and  $4.04 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ , respectively. Thus, the diffusion coefficients of the species in solution can be estimated by using the OCSB theory if the following assumptions are made:

1. The similarity between the electrical conductivities at infinite dilution of the  $\text{Fe}(\text{Cp}^*)_2^+$  and  $\text{Bu}_4\text{N}^+$  cations in  $\text{CH}_2\text{Cl}_2$  at 298.15 K [20], would indicate that the  $\lambda_5/\lambda_1 = 1$  and consequently the Nernst–Einstein relationship leads to  $D_5/D_1 = 1$ .
2. The ion pairs formed by the  $\text{Fe}(\text{Cp}^*)_2^+$  and  $\text{Bu}_4\text{N}^+$  cations with  $\text{PF}_6^-$  would have similar sizes. Therefore, it is expected that their diffusion coefficients satisfy  $D_4 = D_2$  and consequently,  $D_2/D_1 = D_4/D_1 = 1$ .
3. The ratio between the electrical conductivity at infinite dilution of the  $\text{PF}_6^-$  and  $\text{Fe}(\text{Cp}^*)_2^+$  ions in  $\text{CH}_2\text{Cl}_2$  is  $\lambda_3 = 1.77\lambda_1$  [8], and using the Nernst–Einstein relationship, this yields  $D_3/D_1 = 1.77$ .

Thus, the number of parameters of the OCSB theory to be fixed reduces to the ratio  $D_2/D_1$ , the three other ratios being determined by the former assumptions.

The procedure adopted to obtain the  $D_2/D_1$  ratio was to minimize the standard deviation between the experi-

mental  $I^*$  and that calculated with the OCSB theory, resorting to the numerical algorithm recommended by the authors [18]. The best value was  $D_2/D_1 = 0.62$ , yielding  $I^*$  values tabulated in the last column of Table 2. As can be seen in Fig. 3, the OCSB theory describes the limiting currents much better than Eq. (1), which does not include the ion association effects.

In order to obtain the diffusion coefficients of the species in solution we resorted to the expressions of Section 2.2. The diffusion coefficient  $D_2$  of the ion pair ( $\text{Fe}(\text{Cp}^*)_2^+$ ,  $\text{PF}_6^-$ ) was calculated from Eq. (27), using the limiting current for the higher SR ( $1.01 \times 10^3$ , according to Table 2). In our system  $\beta_2 c_E \approx 3$ , in order to get  $D_1$  we used Eq. (26) also using the limiting current for the higher SR. The results are summarized in Table 3. The ratio  $D_2/D_1$  obtained following this procedure was 0.65, in good agreement with the value quoted above obtained by minimization of the standard deviation.

Finally we compare in Table 3 the values of the diffusion coefficients obtained by the application of the OCSB theory with those calculated using the Nernst–Einstein (NE) relationship. From the electric conductivity of the  $\text{Fe}(\text{Cp}^*)_2^+$  ion, we obtain  $D_1 = 1.35 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ , a value smaller than that obtained from the measured limiting current on microelectrodes. The result is not unexpected taking into account that the Nernst–Einstein relationship contains a cation–anion interaction term that is important in low dielectric constant solvents.

The diffusion coefficient of the ion pair quoted in Table 3 is smaller than that of the free ions, which is consistent with the larger size of the ion pair. If we assume that the diffusion of these species in  $\text{CH}_2\text{Cl}_2$  is determined mainly by the viscous friction [22], the Stokes–Einstein relationship leads to:

$$\frac{1}{D_2} = \frac{1}{D_1} + \frac{1}{D_3} \quad (30)$$

which predicts  $D_2 = 1.04 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , in excellent agreement with the value obtained using the limiting current and the OCSB theory.

It is worthwhile to discuss the change of the diffusion coefficients of the decamethylferrocene with the oxidation state and speciation. Diffusion coefficients of  $\text{Fe}(\text{Cp}^*)_2^+$  and  $\text{Fe}(\text{Cp}^*)_2$ , in a variety of solvents, measured with electrochemical techniques are compiled in Table 4.

Due to the presence of methyl groups in the Cp rings of  $\text{Fe}(\text{Cp}^*)_2$ , its molecular size is larger than that of ferrocene, consequently its diffusion coefficient is lower than that reported for ferrocene ( $2.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in acetonitrile [21] and  $2.32 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in dichloromethane [16]). By using the mean value of the  $D\eta$  product ( $0.54 \times 10^{-5} \text{ cm}^2 \text{ mPa}$ ) an effective diameter of 0.81 nm is found for  $\text{Fe}(\text{Cp}^*)_2$ , in solution, which

Table 4  
Diffusion coefficients of ferrocene and decamethylferrocene species at 298 K

Redox species	Solvent	$10^5 D/\text{cm}^2 \text{ s}^{-1}$	$10^5 D\eta/\text{cm}^2 \text{ mPa}$	Ref.
$\text{Fe}(\text{Cp}^*)_2$	Acetonitrile	1.8	0.62	[4]
	Acetonitrile	1.3	0.45	[23]
	Dichloromethane	1.3	0.53	[23]
	Acetophenone	0.32	0.53	[24]
	Nitrobenzene	0.31	0.57	[24]
$\text{Fe}(\text{Cp}^*)_2^+$	Acetonitrile	1.8	0.62	[25]
	Dichloromethane	1.6 <sub>3</sub>	0.67	This work
$(\text{Fe}(\text{Cp}^*)_2^+, \text{PF}_6^-)$	Dichloromethane	1.0 <sub>7</sub>	0.44	This work

is close to the crystallographic diameter, 0.77 nm, calculated from the bond distances [10].

The diffusion coefficient of the  $\text{Fe}(\text{Cp}^*)_2^+$  ion in  $\text{CH}_2\text{Cl}_2$  is in good agreement with that reported in acetonitrile [25] taking into account the different viscosity of the solvents. The effective ion diameter obtained by using the Stokes–Einstein relationship is 0.68 nm, that is, slightly lower than that of the neutral  $\text{Fe}(\text{Cp}^*)_2$  probably because of the solvent structure breaking behavior of this bulky ion.

The ion pair  $(\text{Fe}(\text{Cp}^*)_2^+, \text{PF}_6^-)$ , has a diffusivity lower than that of the neutral and oxidized  $\text{Fe}(\text{Cp}^*)_2$ . This could be explained by the fact that the ion pair is solvent separated [8] and its size is much larger than that of the species  $\text{Fe}(\text{Cp}^*)_2^{0/+}$ .

Thus, the diffusive behavior of the  $\text{Fe}(\text{Cp}^*)_2^{0/+}$  couple in solutions of low permittivity solvents is quite interesting: the diffusivity increases upon oxidation, but it decreases if the  $\text{Fe}(\text{Cp}^*)_2^+$  ion takes part in an association process with the support anion.

## 5. Conclusions

The validity of the OCSB theory for the limiting current at microelectrodes has been tested in dichloromethane, a low permittivity solvent, where the ion pairing effect is well pronounced. The reduction of decamethylferrocenium was studied on a platinum microdisc, using tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Using the association constant of the electroactive and support electrolytes determined in previous work along with reasonable assumptions on the diffusion ratio of several species in the solution, we could verify that the OCSB theory describes accurately the limiting current at different support electrolyte concentrations.

The diffusion coefficients of the  $\text{Fe}(\text{Cp}^*)_2^+$  cation and of the ion pair  $(\text{Fe}(\text{Cp}^*)_2^+, \text{PF}_6^-)$  in  $\text{CH}_2\text{Cl}_2$  were  $1.63 \times 10^{-5}$  and  $1.07 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively, and can be compared to the value  $1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  reported for the neutral  $\text{Fe}(\text{Cp}^*)_2$  in this solvent. The lower value for the ion pair can be explained as the result of its higher

solvodynamic size as compared with the poorly solvated  $\text{Fe}(\text{Cp}^*)_2^+$  and  $\text{PF}_6^-$  ions.

It is expected that microelectrode voltammetry along with OCSB theory could be used as a reliable tool for studying transport processes in supercritical fluids. Our preliminary results [26] on the electrochemistry of ferrocene and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  at a platinum microdisc in supercritical  $\text{CHF}_3$  using  $\text{TBAPF}_6$  as the supporting electrolyte is an indication that this relatively simple technique could become competitive in comparison with more sophisticated methods used to study transport properties in such a complex fluid.

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