

# Electrochemistry in supercritical trifluoromethane

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## Abstract

The use of trifluoromethane ( $\text{CHF}_3$ ) as a solvent for electrochemical studies in supercritical conditions is analyzed. The dielectric and electrical conductivity of supercritical  $\text{CHF}_3$  was measured at 323.15 K at several densities. The solubility and electrical conductivity of tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) and decamethylferrocenium hexafluorophosphate ( $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ ) in supercritical  $\text{CHF}_3$  were measured at 323.15 K as a function of density. It was found that, in spite of the high ion pair formation of the  $\text{TBAPF}_6$  in the supercritical solvent, this salt is a suitable supporting electrolyte, having a conductivity much higher than that reported for other electrolytes in low dielectric constant supercritical solvents. The limiting currents measured for decamethylferrocene ( $\text{Fe}(\text{Cp}^*)_2$ ) and decamethylferrocenium hexafluorophosphate ( $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ ) at a platinum microdisc in supercritical  $\text{CHF}_3$  at several densities and 323.15 K, show the feasibility of using the proposed supercritical system as a model for electrochemical studies in variable density media. The effect of concentration of the supporting electrolyte on the limiting current at the microelectrode is qualitatively discussed in terms of a recent theory which takes into account the ion association of the supporting and electroactive electrolytes. © 2000 Published by Elsevier Science S.A.

**Keywords:** Supercritical trifluoromethane; Electrical conductivity; Decamethylferrocenium hexafluorophosphate; Tetrabutylammonium hexafluorophosphate; Limiting current; Microelectrodes

## 1. Introduction

There is an increasing interest in the study of transport processes in supercritical solvents, since these fluids exhibit high mass transfer coefficients and they are potentially useful for several industrial applications.

One of the simplest electrochemical techniques to study diffusion coefficients in fluids is linear sweep voltammetry. The voltammetric measurement of the limiting current using microelectrodes seems adequate in supercritical fluids because the low dielectric constant of these fluids severely limit the solubility of salts. The technique yields reliable results only if microelectrodes are used due to the high resistivity of the supercritical solution.

Carbon dioxide is the most commonly used supercritical solvent. Niehaus et al. [1] studied the oxidation of ferrocene using tetrahexylammonium hexafluorophosphate ( $\text{THAPF}_6$ ) as supporting electrolyte.  $\text{THAPF}_6$  reduced the ohmic distortion of the voltammograms, but its concentration was so high that liquid–liquid phase separation was observed. Only the addition of a small amount of water allowed the authors to perform reliable electrochemistry experiments. However, the mixture  $\text{CO}_2$ – $\text{H}_2\text{O}$  is quite complex as a solvent to analyze transport properties.

More recently, Abbot and Harper [2] used a hydrophobic salt, tetradecylammonium tetraphenylborate ( $\text{TDABPh}_4$ ) as supporting electrolyte in supercritical  $\text{CO}_2$ . The specific conductivity of this solution is very low in the range of pressure studied (5–30 MPa) and the voltammograms showed the typical distortion of highly resistive media. In addition, the lack of information on the solubility and aggregation state of the long chained molecules introduced some uncertainty on the ability of supercritical  $\text{CO}_2$  to truly solvate this salt without micelle formation.

Olsen and Tallman [3,4] studied the electrochemistry of ferrocene and cobaltocenium hexafluorophosphate in

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chlorodifluoromethane ( $\text{ClF}_2\text{CH}$ ), a solvent with critical parameters  $T_c = 369.2$  K and  $p_c = 4.97$  MPa, having a good solubility for tetrabutylammonium tetrafluoroborate ( $\text{TBABF}_4$ ). The concentration of the solutions reached  $0.012$  mol  $\text{dm}^{-3}$  in the 10–24 MPa pressure range (densities between  $0.81$  and  $1.02$  g  $\text{cm}^{-3}$ ). The voltammograms showed almost no ohmic distortion and can be considered as the first electrochemical experiments carried out in a supercritical fluid of low dielectric constant.

Abbott et. al. [5] used 1,1,1,2-tetrafluoroethane ( $\epsilon_c = 3.5$ ) and difluoromethane ( $\epsilon_c = 4.9$ ) as solvents of higher relative permittivities at the critical point compared to  $\text{ClF}_2\text{CH}$  ( $\epsilon_c = 2.31$ ). With  $\text{TBAClO}_4$  as supporting electrolyte these solvents can be used to study electrochemical process at large positive overpotentials, but no transport properties of ions have been reported in these solvents yet.

It should be noted that Bard and coworkers have studied several supercritical fluids of high dielectric constant, such as  $\text{NH}_3$  [6,7],  $\text{SO}_2$  [8],  $\text{H}_2\text{O}$  [9,10] and  $\text{CH}_3\text{CN}$  [11,12] obtaining diffusion coefficients of several solutes at different densities using cyclic voltammetry, chronoamperometry and cronocoulometry.

The advantage of choosing CFCs or HFCs as solvents for electrochemical experiments with supercritical fluids rely on the conjunction of several features: mild critical parameters ( $P_c$ ,  $T_c$ ) when compared to  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$ , which make them easier to operate experimentally; potential window larger than  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  (due to its inertness towards oxidation/reduction), thus extending the variety of solutes available for studies in such solvents, and the possibility of dissolving significant amounts of salts composed of bulky ions of low charge/radius ratio

due to its non-zero dipolar moment. The most popular supercritical fluid,  $\text{CO}_2$ , is known for its poor solvent power towards polar and ionic compounds. A polar HFC like  $\text{CHF}_3$  appears as a valuable fluid to study transport properties of ions in variable-density solvents of low dielectric constant.

Electrochemical experiments with charged redox species in organic solvents have been traditionally performed without considering the possibility of ion association to form ion pairs in those cases where the dielectric constant of the solvent is low enough to stabilize the free ion. In this work, information of transport properties of tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , supporting electrolyte) and decamethylferrocenium hexafluorophosphate ( $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ , electroactive species) in supercritical  $\text{CHF}_3$  was obtained using electrical conductance and linear sweep voltammetry with microelectrodes.

## 2. Experimental

Trifluoromethane (K.H.Muller Laboratories, > 99%) was stored in a stainless steel cylinder ( $200$  cm<sup>3</sup>) containing KOH in order to eliminate traces of water. After used  $\text{CHF}_3$  was stored in a similar cylinder and it was recovered by distillation at  $-78^\circ\text{C}$  (acetone– $\text{CO}_2$  mixture). The  $\text{CHF}_3$  was received in a cylinder containing KOH, immersed in liquid nitrogen.

$\text{TBAPF}_6$  (Fluka, electrochemical grade) was used as received.  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  was synthesized and purified following a literature procedure [13]. The solid was dried at  $110^\circ\text{C}$  during 12 h and was used without recrystallization. All solids were stored in a vacuum desiccator.

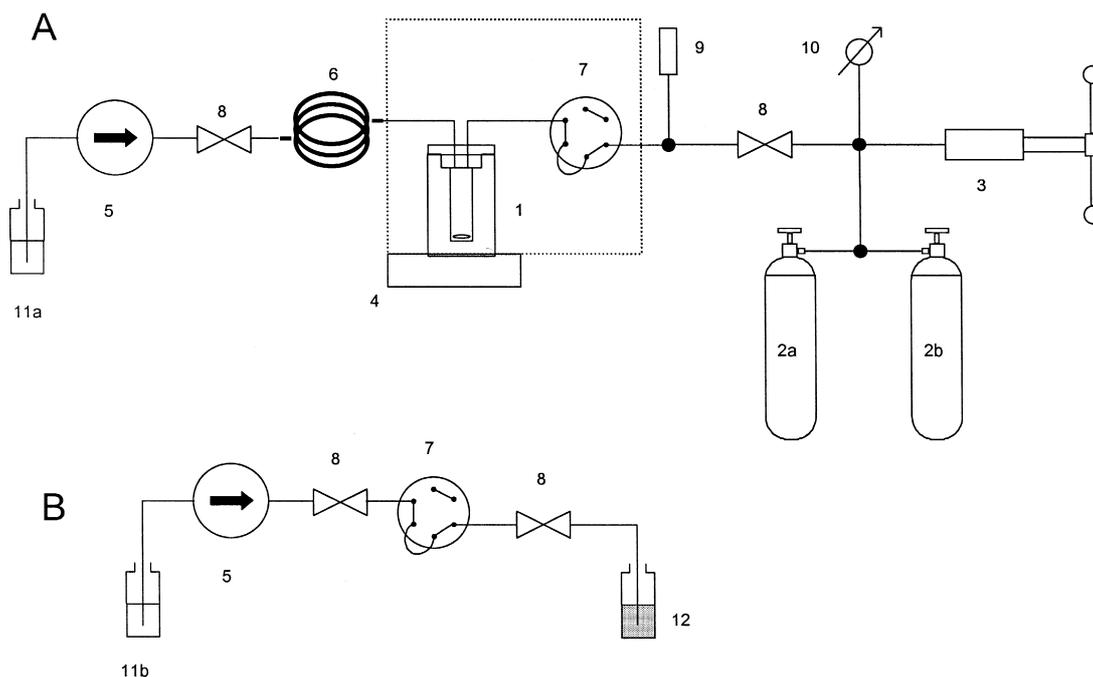


Fig. 1. Block diagram of the experimental setup for the solubility measurements (see text for the references).

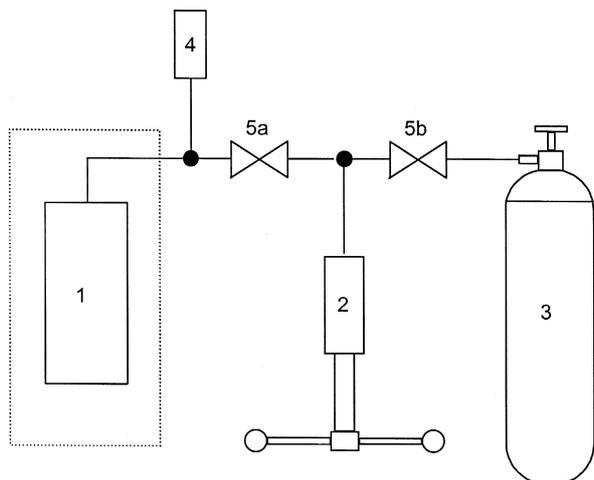


Fig. 2. Block diagram of the experimental setup for dielectric constant and electrical conductivity measurements (see text for references)

The experimental setup employed to measure the solubility of  $\text{TBAPF}_6$  and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in  $\text{CHF}_3$  is shown in Fig. 1. The sampling step is illustrated in A, where the stainless steel equilibration cell (1) containing an excess of the solid salt and the six ports valve (7) were thermostated at 323 K. Once vacuum is made in the system,  $\text{CHF}_3$  (2a) is filled into the cell by means of a high pressure manual pump (3). A pressure transducer (9) and a gauge manometer (10) were used to control the pressure of the system. The equilibrium is reached after several hours under stirring (4). Afterwards, water (11a) is pumped by the HPLC pump (5) through the loop (6) containing mercury, which acts as a piston to displace the content of the cell through a sampling loop connected to the six port valve. A micrometric valve (8) is used to vent the fluid at a very low flow rate ( $0.05 \text{ cm}^3/\text{min}$ ). The  $\text{CHF}_3$  is condensed in the cylinder (2b) immersed in liquid nitrogen.

After a considerable volume of solution has been flushed through the sampling loop, it is insulated by switching the six port valve and the configuration of the system is changed to that indicated in B. The salt deposited on the line is removed by circulating 1,2-dichloroethane (11b) through the six port valve. This liquid is dismissed and the six port valve is switched to the original position, connecting the sampling loop to the rest of the line. The content of the sampling loop is pushed with 1,2-dichloroethane through the valve (8) and stored in a glass vessel (12) having a total volume of  $10 \text{ cm}^3$ .

The analytical determination of the solubility was performed by placing the sample in contact with an aqueous solution of methylene blue. The absorbance of the reaction product at 657 nm was used to calculate the analytical concentration of the hexafluorophosphate anion in conjunction with a calibration curve

The high pressure cell used for the conductivity measurements and for the determination of the dielectric constant of  $\text{CHF}_3$  as a function of pressure has been described

elsewhere [14]. The constant of the cell ( $0.27457 \text{ m}^{-1}$ ) was determined by measuring its capacitance under vacuum. The experimental setup for these measurements are shown in Fig. 2. The solute dissolved in dichloroethane is charged into the cell (1) by means of a syringe using an inlet not shown in Fig. 2. The solvent is evaporated under vacuum and the cell is thermostated at 323 K.  $\text{CHF}_3$  in cylinder (3) is charged in the high-pressure manual pump (2) through the valve (5b) keeping valve (5a) closed. Then, valve (5a) is open and the high-pressure pump is used to increase the  $\text{CHF}_3$  pressure to the selected value measured with the pressure transducer (4).

The electrochemical cell for measurements at high pressure is shown in Fig. 3. It was built in titanium and the upper part contains the working electrode (1), a platinum

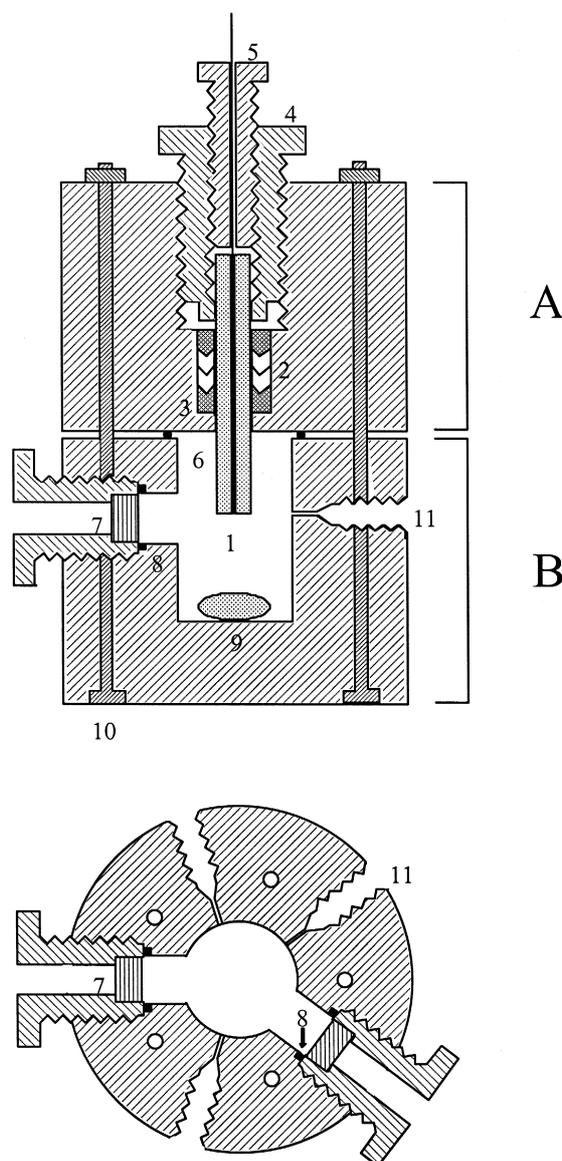


Fig. 3. Schematic diagram of the high-pressure electrochemical cell. Top: lateral view of the upper and bottom parts. Bottom: top view of the bottom part (see text for references).

Table 1  
Dielectric constant of supercritical CHF<sub>3</sub> at 323.15 K

$\rho$ (g cm <sup>-3</sup> )	$\epsilon$
0.2082	1.6 <sub>6</sub>
0.2940	1.9 <sub>9</sub>
0.4130	2.5 <sub>4</sub>
0.4932	2.9 <sub>7</sub>
0.5825	3.4 <sub>7</sub>
0.7200	4.3 <sub>4</sub>
0.8155	5.0 <sub>1</sub>
0.8697	5.4 <sub>2</sub>
0.9115	5.7 <sub>6</sub>

disc 25  $\mu$ m in diameter, encapsulated in soft glass 6 mm in diameter. The pressure seal is performed by PTFE chevron gasket (2) and titanium gasket (3). A compression nut (4) and a security bolt (5) complete the pressure seal of the microelectrode.

The bottom part contains two sapphire windows (7) 15 mm in diameter with PTFE o-rings (8) as pressure seals, which allow the inspection of the cell inside. A silver wire (Goodfellow) 1 mm in diameter (not shown in Fig. 3) was used as pseudo-reference electrode, wrapped around the working electrode.

The cell is filled with CHF<sub>3</sub> through one of the input port (11), with HPLC piping (PEEK) of 1/16" external diameter. The cell parts are tight together by means of five stainless steel bolts (10), with a gold o-ring (6) 30 mm in diameter and 0.5 mm thick acting as pressure sealing. The cell is stirred by using a magnetic bar (9). The total volume of the electrochemical chamber is 9.26 cm<sup>3</sup>.

A Wayne Kerr 6425 Component Analyzer was used for measuring the capacitance and resistance of the fluids under study, by applying a 0.1 V sinusoidal signal in the range between 500 Hz and 10 kHz.

A potentiostat (Oxford Instruments) designed for low current applications (pA) and connected to a PC through a IEEE-488 interface was used to generate the voltage signal and measure the current.

### 3. Results and discussion

#### 3.1. Properties of supercritical CHF<sub>3</sub>

The critical parameters of the CHF<sub>3</sub> are  $T_c = 299.3$  K,  $p_c = 4.858$  MPa and  $\rho_c = 0.529$  g cm<sup>-3</sup>. The density of

CHF<sub>3</sub> at 323.15 K as a function of pressure was taken from the data by Rubio et al. [15] and the viscosity was reported by Altunin *et al* [16]. The dielectric constant of CHF<sub>3</sub> was measured by Reuter et al. [17] above the critical temperature up to 468 K and 200 MPa. Due to the scarce experimental points reported in the range of experimental conditions of interest in this work, we measured the dielectric constant using the high-pressure stainless steel cell. The dielectric constant was obtained from the ratio between the capacitance of the fluid and the capacitance under vacuum.

Table 1 summarizes the values obtained at 323.15 K and pressures between 5 and 16 MPa. The dielectric constant can be expressed as:

$$\epsilon = 0.9447 + 2.9343\rho + 2.0885\rho^2 + 0.5299\rho^3 \quad (1)$$

in the range of density between 0.21 and 0.91 g cm<sup>-3</sup> with standard deviation,  $\sigma = 0.008$ .

#### 3.2. Solubility of TBAPF<sub>6</sub> and Fe(Cp<sup>\*</sup>)<sub>2</sub>PF<sub>6</sub> in CHF<sub>3</sub>

Table 2 shows solubility data obtained for the supporting electrolyte (TBAPF<sub>6</sub>) and the electroactive electrolyte (Fe(Cp<sup>\*</sup>)<sub>2</sub>PF<sub>6</sub>). It is observed that the solubility increases exponentially with the density and for both salts it can be expressed as:

$$\log s = a + b\rho \quad (2)$$

where  $a = -7.06$ ,  $b = 6.44$  for TBAPF<sub>6</sub> ( $\sigma = 0.012$ ) and  $a = -8.34$ ,  $b = 6.56$  for Fe(Cp<sup>\*</sup>)<sub>2</sub>PF<sub>6</sub>, ( $\sigma = 0.009$ ) with  $s$  in mol dm<sup>-3</sup> and  $\rho$  in g cm<sup>-3</sup>.

#### 3.3. The electrical conductivity of salts in supercritical CHF<sub>3</sub>

We first determined the conductivity of pure supercritical CHF<sub>3</sub> at 323.15 K in the range of density between 0.294 and 0.915 g cm<sup>-3</sup>. The results for the specific conductance,  $\kappa^0$ , summarized in Table 3 could be expressed in the polynomial form:

$$\log \kappa^0 = -20.7470 + 44.1610\rho - 81.4748\rho^2 + 90.7700\rho^3 - 40.0522\rho^4 \quad (3)$$

where  $\kappa^0$  is in S cm<sup>-1</sup> and  $\rho$  in g cm<sup>-3</sup> (standard deviation  $\sigma = 0.03$ ).

The conductivity of TBAPF<sub>6</sub> in supercritical CHF<sub>3</sub> at 323.15 K was measured in the range of density 0.29–0.91

Table 2  
Solubility of TBAPF<sub>6</sub> and Fe(Cp<sup>\*</sup>)<sub>2</sub>PF<sub>6</sub> in supercritical CHF<sub>3</sub> at 323.15 K

$P$ (bar)	$\rho$ CHF <sub>3</sub> (g cm <sup>-3</sup> )	$s$ TBAPF <sub>6</sub> (mol dm <sup>-3</sup> )	$P$ (bar)	$\rho$ CHF <sub>3</sub> (g cm <sup>-3</sup> )	$s$ Fe(Cp <sup>*</sup> ) <sub>2</sub> PF <sub>6</sub> (mol dm <sup>-3</sup> )
71.1	0.415	$4.15 \times 10^{-5}$	76.66	0.497	$8.2 \times 10^{-6}$
89.7	0.656	$1.39 \times 10^{-3}$	96.53	0.707	$2.1 \times 10^{-4}$
160.9	0.913	$6.68 \times 10^{-2}$	157.53	0.906	$4.0 \times 10^{-3}$

Table 3  
Specific conductivity of supercritical  $\text{CHF}_3$  at 323.15 K

$P$ (bar)	$\rho$ ( $\text{g cm}^{-3}$ )	$\kappa^0$ ( $\text{S cm}^{-1}$ )	$\Delta\kappa^0/\kappa^0$
160.51	0.9155	$8.51 \times 10^{-8}$	-0.048
139.54	0.8697	$6.28 \times 10^{-8}$	0.078
119.60	0.8155	$3.83 \times 10^{-8}$	0.031
98.52	0.7200	$9.47 \times 10^{-9}$	-0.104
82.92	0.5825	$4.29 \times 10^{-10}$	0.067
76.40	0.4932	$5.26 \times 10^{-11}$	0.032
70.96	0.4130	$7.04 \times 10^{-12}$	-0.054
61.34	0.2940	$1.57 \times 10^{-13}$	0.013

$\text{g cm}^{-3}$  and the results are shown in Table 4. Also shown in this table are the conductivities of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in supercritical  $\text{CHF}_3$  in the range of density 0.45–0.91  $\text{g cm}^{-3}$ . The concentration of the salts were  $6.511 \times 10^{-4}$   $\text{mol dm}^{-3}$  and  $6.135 \times 10^{-5}$   $\text{mol dm}^{-3}$  for  $\text{TBAPF}_6$  and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ , respectively. In both cases the solutions become saturated at low densities and the corresponding saturation concentrations were calculated using Equation (2).

In order to avoid the effect of concentration,  $c$ , in the comparison of the conductivity, in Fig. 4 we plotted the molar conductivity ( $\Lambda = \kappa/c$ ) of both salts in supercritical  $\text{CHF}_3$  as a function of density. It is clear that the molar conductivity of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  is higher than that of  $\text{TBAPF}_6$ . That means that the association constant of  $\text{TBAPF}_6$  in supercritical  $\text{CHF}_3$  at a given density is higher than the association constant of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ .

A high association of the supporting electrolyte is not wished for performing electrochemical measurements in supercritical fluids. However, it should be emphasized that

Table 4  
Specific conductivity of  $\text{TBAPF}_6$  and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in  $\text{CHF}_3$  at 323.15 K.

$c$ $\text{TBAPF}_6$ ( $\text{mol dm}^{-3}$ )	$P$ (bar)	$\rho$ ( $\text{g cm}^{-3}$ )	$\kappa$ ( $\text{S cm}^{-1}$ )
$6.511 \times 10^{-4}$	158.88	0.9086	$1.76 \times 10^{-5}$
	132.33	0.8518	$1.25 \times 10^{-5}$
	117.35	0.8068	$8.80 \times 10^{-6}$
	105.19	0.7566	$5.81 \times 10^{-6}$
	96.77	0.7088	$3.84 \times 10^{-6}$
	91.05	0.6660	$2.61 \times 10^{-6}$
	85.44	0.6118	$1.56 \times 10^{-6}$
	81.75	0.5678	$6.86 \times 10^{-7}$
$(3.92 \times 10^{-4})$	78.09	0.5179	$2.19 \times 10^{-7}$
$(1.87 \times 10^{-4})$	74.24	0.4612	$4.62 \times 10^{-8}$
$c$ $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$ ( $\text{mol dm}^{-3}$ )	$P$ (bar)	$\rho$ ( $\text{g cm}^{-3}$ )	$\kappa$ ( $\text{S cm}^{-1}$ )
$6.135 \times 10^{-5}$	156.31	0.9040	$1.30 \times 10^{-5}$
	133.92	0.8559	$1.04 \times 10^{-5}$
	117.27	0.8065	$7.83 \times 10^{-6}$
	104.80	0.7547	$5.48 \times 10^{-6}$
	96.85	0.7094	$3.80 \times 10^{-6}$
	91.01	0.6657	$2.44 \times 10^{-6}$
	85.50	0.6125	$1.12 \times 10^{-6}$
	81.61	0.5660	$4.53 \times 10^{-7}$
	77.93	0.5156	$1.46 \times 10^{-7}$
	73.68	0.4528	$2.74 \times 10^{-8}$
$(4.76 \times 10^{-5})$			
$(2.36 \times 10^{-5})$			
$(1.10 \times 10^{-5})$			
$(4.26 \times 10^{-6})$			

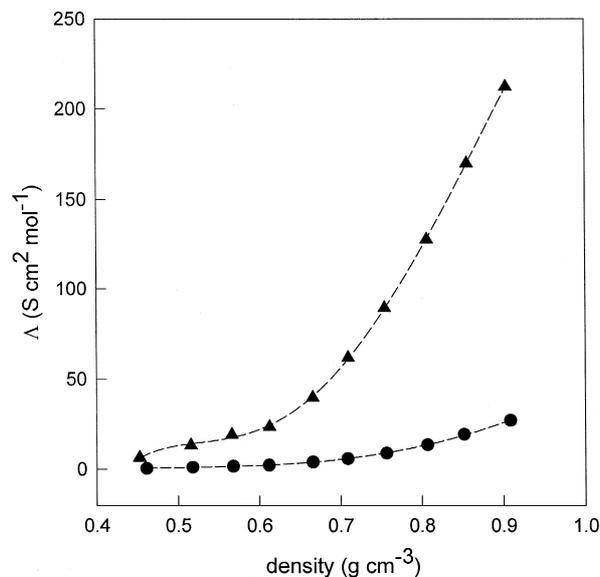


Fig. 4. Molar conductivity of  $\text{TBAPF}_6$  (●) and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  (▲) in  $\text{CHF}_3$  as a function of density at 323.15 K.

this kind of behavior is expected for all the supercritical solvents having low dielectric constant. The corresponding state theory [18] predicts that the association constant of formation of ion pairs is proportional to the inverse of the reduced temperature, defined as:

$$b^* = \frac{|z_+ z_-|}{\epsilon k T \sigma} e^2 \quad (4)$$

where  $\sigma$  is the effective diameter of the ions.

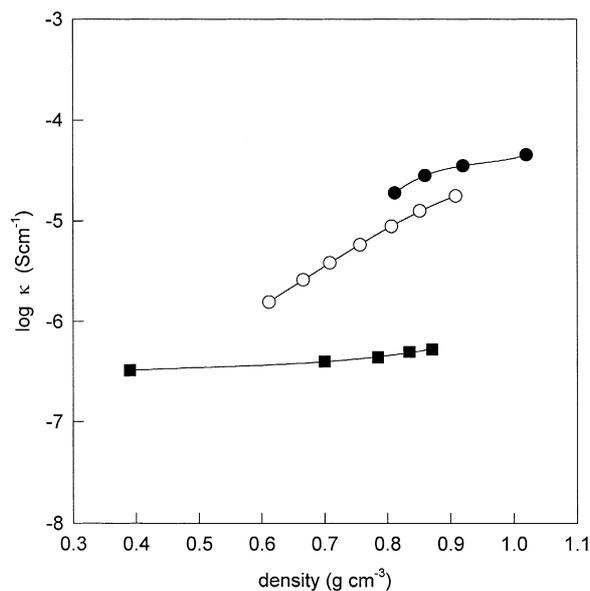


Fig. 5. Specific conductivity of salts in supercritical solvents: (○)  $\text{TBAPF}_6/\text{CHF}_3$  at 323.15 K,  $c = 6.51 \times 10^{-4}$   $\text{mol dm}^{-3}$ ; (●)  $\text{TBAPF}_6/\text{CHClF}_2$  at 388 K,  $c = 1 \times 10^{-2}$   $\text{mol dm}^{-3}$  [4]; (■)  $\text{TDABPh}_4/\text{CO}_2$  at 323 K,  $c = 1.92 \times 10^{-2}$   $\text{mol dm}^{-3}$  [2].

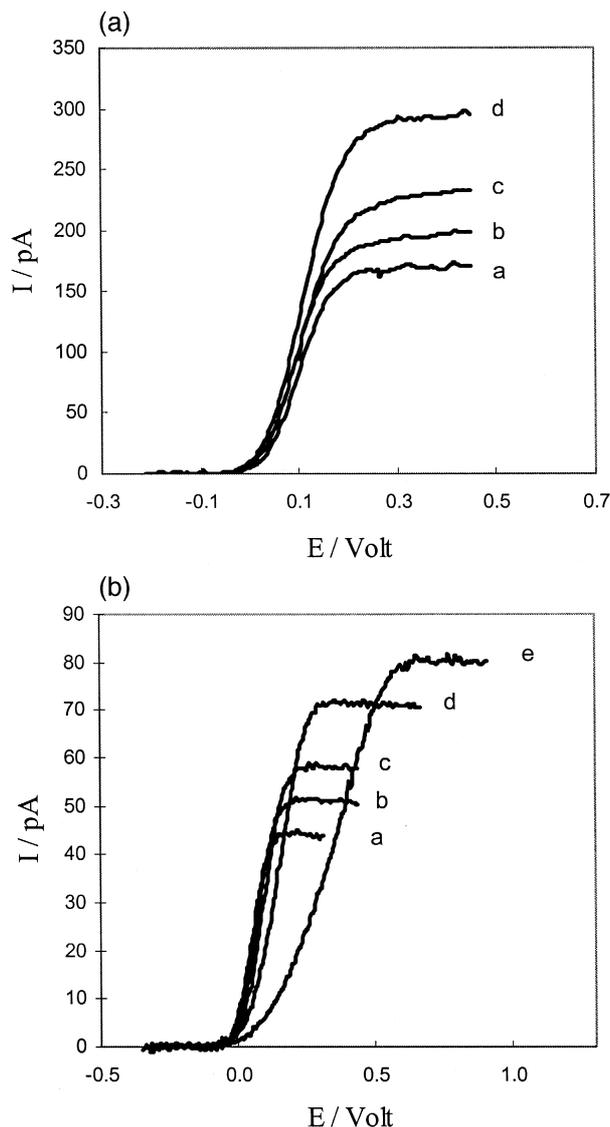


Fig. 6. Linear sweep voltammograms of decamethylferrocene at a  $25\ \mu\text{m}$  Pt disc microelectrode in supercritical  $\text{CHF}_3$  at 323.15 K; (6a) with supporting electrolyte ( $c_E = 4.83 \times 10^{-6}\ \text{mol dm}^{-3}$ ,  $c_S = 4.8 \times 10^{-4}\ \text{mol dm}^{-3}$ ); (6b) without supporting electrolyte ( $c_E = 4.83 \times 10^{-6}\ \text{mol dm}^{-3}$ ). Densities (in  $\text{g cm}^{-3}$ ): (a) 0.905; (b) 0.805; (c) 0.708; (d) 0.602; and (e) 0.508. Scan rate: 5 mV/s.

An estimation of the association constant of  $\text{TBAPF}_6$  in  $\text{CHF}_3$  at 323.15 K (assuming  $\sigma = 0.79\ \text{nm}$ ) using the cluster theory of electrolytes [19] predicts that the association constant increases from  $6 \times 10^4$  to  $7 \times 10^8$  when the density decreases from 0.9 to  $0.5\ \text{g cm}^{-3}$ . Nevertheless, it should be noted that the specific conductivity of  $\text{TBAPF}_6$  in  $\text{CHF}_3$  at 323.15 K is much higher than that measured for  $\text{TDABPh}_4$  in  $\text{CO}_2$  at the same temperature [2] over the entire range of density and it is slightly lower than that reported by Olsen and Tallman [3] for  $\text{TBAPF}_6$  in  $\text{CHClF}_2$  at 388 K and concentration  $c = 10^{-2}\ \text{mol dm}^{-3}$ , as shown in Fig. 5. This result can only be explained by assuming that  $\text{TBAPF}_6$  is much more associated in  $\text{CHClF}_2$  than in  $\text{CHF}_3$ . The dielectric constant of  $\text{CHClF}_2$  is lower than

Table 5

Slope of a plot of  $E\ (\text{mV})$  vs.  $\log[(I(SR \rightarrow \infty) - I)/I]$  for the oxidation of  $\text{Fe}(\text{Cp}^*)_2$  in supercritical  $\text{CHF}_3$  at 323.15 K and several densities. Values in mV.

Density ( $\text{g cm}^{-3}$ )	Excess of supporting electrolyte ( $SR = 100$ )	Absence of supporting electrolyte
0.508	–	192
0.603	72	116
0.708	69	92
0.805	65	91
0.905	66	89

that of  $\text{CHF}_3$  and this difference could account for the observed behavior. Thus, we have characterized a system formed by  $\text{CHF}_3$  as supercritical solvent and  $\text{TBAPF}_6$  as supporting electrolyte, which has promising features as a supercritical media for electrochemical experiments.

### 3.4. Steady state voltammetry in supercritical $\text{CHF}_3$

Steady state voltammetry experiments were carried out in supercritical  $\text{CHF}_3$ . Fig. 6 shows the current vs. voltage curves for decamethylferrocene ( $\text{Fe}(\text{Cp}^*)_2$ ) in supercritical  $\text{CHF}_3$  at 323.15 K at several densities with and without supporting electrolyte. It is interesting to note that even in the complete absence of supporting electrolyte (Fig. 6b) the shape of the voltammogram is still preserved, and despite the large ohmic drop observed the analysis of the limiting current obtained from the curve does not lose accuracy. This fact plays an important role when it is necessary to add migrational processes to the diffusional current at microelectrodes.

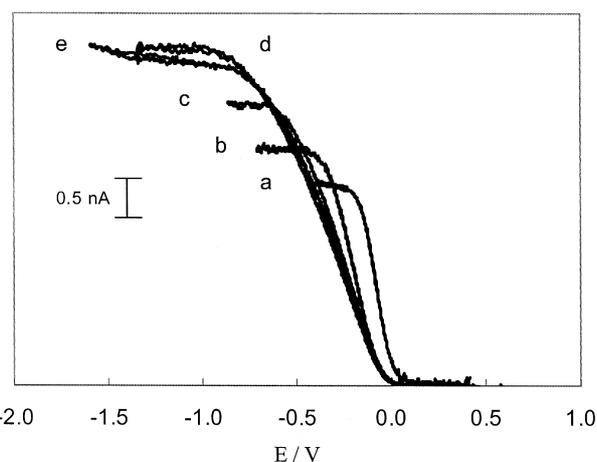


Fig. 7. Linear sweep voltammograms of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in supercritical  $\text{CHF}_3$  at 323.15 K and density  $0.65\ \text{g cm}^{-3}$  at several concentrations of  $\text{TBAPF}_6$ : (a)  $5.1 \times 10^{-4}$ ; (b)  $5.15 \times 10^{-4}$ ; (c)  $5.25 \times 10^{-5}$ ; (d)  $5.0 \times 10^{-6}$ ; and (e)  $5.0 \times 10^{-7}\ \text{mol dm}^{-3}$ . The concentration of  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  is  $5.0 \times 10^{-5}\ \text{mol dm}^{-3}$ , except in case (a) where  $c_E = 5.0 \times 10^{-6}\ \text{mol dm}^{-3}$ . Current in curve (a) was multiplied by 10 for better comparison with other curves. Scan rate: 5 mV/s.

Table 6

Limiting current for the reduction of and  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in supercritical  $\text{CHF}_3$ , density  $0.65 \text{ g cm}^{-3}$ , at 323.15 K.

$c_s$ (mol/dm <sup>3</sup> )	$c_l$ (mol/dm <sup>3</sup> )	$I_L$ (nA)	$I_L^{\text{norm}}$ (nA mol/dm <sup>3</sup> )	$I^*$ (experimental)
$5.1 \times 10^{-4}$	$5.0 \times 10^{-6}$	0.24	$4.8 \times 10^4$	1.00
$5.15 \times 10^{-4}$	$5.0 \times 10^{-5}$	2.8	$5.6 \times 10^4$	1.17
$5.25 \times 10^{-5}$	$5.0 \times 10^{-5}$	3.3	$6.6 \times 10^4$	1.38
$5.0 \times 10^{-6}$	$5.1 \times 10^{-5}$	4.1	$8.0 \times 10^4$	1.67
$5.0 \times 10^{-7}$	$5.0 \times 10^{-5}$	3.9	$7.8 \times 10^4$	1.63

The extent of the ohmic drop (IR) was obtained from the slope of a plot  $E$  vs.  $\log[(I(SR \rightarrow \infty) - I)/I]$ . A value of 64.1 mV is predicted for the exchange of a single electron under reversible conditions at 323.15 K. As it can be seen in Table 5, the oxidation of  $\text{Fe}(\text{Cp}^*)_2$  proceeds reversibly, while the low conductivity of the medium generates an ohmic drop (IR) that increases with the decrease in density. For the case of excess of supporting electrolyte, this is due to the lower dielectric constant of the solvent at lower densities, that leads to a higher degree of association and consequently less free ions from the supporting electrolyte. In the case of absence of added supporting electrolyte, impurities coming from the solvent contribute to some extent to the conductivity of the medium. The concentration of those charge carriers scale with the solvent density and are expected to be more associated at low densities for the same reasons explained above.

Fig. 7 shows the voltammetric curves for  $\text{Fe}(\text{Cp}^*)_2\text{PF}_6$  in  $\text{CHF}_3$  at 323.15 K and density  $0.65 \text{ g cm}^{-3}$  at different concentrations of supporting electrolyte (the concentration of the electroactive electrolyte is:  $c_E = 5 \times 10^{-6}$ , curve a;  $c_E = 5 \times 10^{-5}$ , curves b–e).

In this case the reduction of the  $\text{Fe}(\text{Cp}^*)_2^+$  cation is strongly influenced by the concentration,  $c_s$ , of supporting electrolyte. We have proved recently [20] in low dielectric constant solvents that the theory by Oldham et al. [21] (OCSB theory) is able to describe the effect of strong ionic association in systems containing variable concentration of supporting electrolyte.

The reduced current  $I^*$ , defined by:

$$I^* = \frac{I_l^{\text{norm}}(SR)}{I_l^{\text{norm}}(SR \rightarrow \infty)} \quad (5)$$

where  $I_l^{\text{norm}} = I_l/c_E$  and  $SR = c_s/c_E$  (supporting ratio), shows the qualitative behavior predicted by the OCSB theory. The theory describes the dependence of  $I^*$  on the diffusion coefficient of the several species present in a media with strong ion-pair formation and on the association constants of the supporting and electroactive electrolytes.

Table 6 clearly shows how the decrease in concentration of supporting electrolyte increases the limiting current, due to the increases of the migrational current.

A more complete analysis of the OCSB theory in supercritical fluids is underway using the reduction of  $\text{Fe}(\text{Cp}^*)_2^+$  in supercritical  $\text{CHF}_3$  as a model system.

#### 4. Conclusions

Trifluoromethane, a solvent with accessible critical point ( $T_c = 299.3 \text{ K}$ ,  $\rho_c = 0.529 \text{ g cm}^{-3}$ ), and a low dielectric constant ranging from 1.6 at  $\rho = 0.2 \text{ g cm}^{-3}$  to 5.7 at  $\rho = 0.9 \text{ g cm}^{-3}$  at 323.15 K, seems suitable for electrochemical studies under supercritical conditions.

The solubility and electrical conductivity of  $\text{TBAPF}_6$  in supercritical  $\text{CHF}_3$  is high enough to provide supporting ions for diffusion coefficient measurements by determining limiting currents on microelectrodes, even taking into account the strong ion association of this salt in the low density supercritical  $\text{CHF}_3$ .

A high-pressure electrochemical cell with a platinum microdisc electrode has been used to obtain limiting currents for the oxidation of decamethylferrocene and the reduction of the  $\text{Fe}(\text{Cp}^*)_2^+$  cation in supercritical  $\text{CHF}_3$ . The limiting currents are influenced by the concentration of supporting  $\text{TBAPF}_6$  in the way predicted by the OCSB theory [21]. Thus, the reduced limiting current increases with the decreases of the supporting ratio  $SR$  due to the increases of the migrational current.

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