Mechanism of the electrochemical reduction of sulfur dioxide in non-aqueous solvents

Elisabeth Potteau a, Eric Levillain b, Jean-Pierre Lelieur a,*

a Laboratoire de Spectrochimie Infrarouge et Raman (LASIR, UMR 8516 CNRS), Hautes Etudes Industrielles (HEI), 13 rue de Toul, 59046 Lille Cedex, France
b Ingénierie Moléculaire et Matériaux Organiques (IMMO, UMR 6501 CNRS), Université d’Angers, 2 boulevard Lavoisier, 49045 Angers Cedex, France

Received 11 May 1999; received in revised form 2 August 1999; accepted 3 August 1999

Abstract

The results of the spectroscopic and electrochemical study of SO2 solutions and of polythionite solutions (i.e. solutions where SO2 is reduced chemically) in HMPA, allowed us to build a model describing the reduction of SO2 in non-aqueous solvents. Simulations and adjustments of this model to the experimental data led to the determination of the parameters of the reactions. This mechanism is shown to explain the observations for all solutions, both in semi-infinite diffusion and in thin layer conditions, and it also describes the composition of any polythionite solution. The model also explains the reduction of SO2 in other non-aqueous solvents. The analysis of the mechanism shows that the stability and electroactivity of the species involved can be related to their structure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Sulfur dioxide; Non-aqueous solvent; Reduction; Redox mechanism; Cyclic voltammetry; Digisim®

1. Introduction

The sulfur dioxide radical anion, SO2−, is widely used as a reagent in organic electrosynthesis [1,2]. Moreover, lithium batteries now often contain SO2 as an additive [3], which is reduced during the battery operation. However, the reduction of SO2 in non-aqueous solvents is not a simple one-electron transfer, and several follow-up reactions occur, including other electron transfers. For an efficient use of the reduction of SO2, a good understanding of all other reactions taking place is required.

For that purpose, two main directions have been investigated: the electrochemical study of SO2 solutions [4–13], and the spectroscopic study of electrolyzed solutions [5,7,11,12,14–17].

A typical voltammogram of a SO2 solution consists of one major reduction peak, and at least two oxidation peaks (Fig. 1). All authors agree that in non-aqueous solvents, the reduction of SO2 is mono-electronic, and leads to the formation of the SO2− radical:

SO2 + e− ⇌ SO2− (1)

The main reduction peak (Fig. 1) has been unanimously assigned to this reaction. Most of the authors observe two oxidation peaks, but some have identified three or four peaks [4,5]. Adsorption phenomena occur frequently [6–8,10], leading to difficulties in the interpretation. Moreover, Hg electrodes were used in some studies [4,9,10], but Hg was shown later [11] not to be inert towards the reduction products.

The first oxidation peak is assigned to the oxidation of SO2 in most studies [4–13]. The identification of the other oxidation peaks (between one and three peaks) is more controversial. However, these are obviously the oxidation of species formed through follow-up reactions. Several species have been identified during the spectroscopic study of electrolytically reduced solutions. It is generally agreed that SO2− can dimerize, giving the dithionite ion S2O42− [4–10,12,13]:

2 SO2− ⇌ S2O42− (2)
A second stable radical species was identified as (SO_2)_2SO_4^{1-} [5,7,9–17], but the value of x has long been uncertain. However, since the work of Gardner et al. [9], it is accepted that x = 1, giving the formula S_2O_4^{2-}. This species results from the reaction of SO_2^{+} with SO_2:

\[
\text{SO}_2 + \text{SO}_2^{+} \rightleftharpoons \text{S}_2\text{O}_4^{2-} \quad (3)
\]

The existence of a ‘red complex’, S_3O_6^{2-}, is also mentioned in a few studies [4,5,11,12,17]. It can be formed by two reactions [11,12]:

\[
\text{S}_2\text{O}_4^{2-} + \text{SO}_2^{+} \rightleftharpoons \text{S}_3\text{O}_6^{2-} \quad (4)
\]

\[
\text{SO}_2 + \text{S}_2\text{O}_4^{2-} \rightleftharpoons \text{S}_3\text{O}_6^{2-} \quad (5)
\]

In addition to the formation of these species, several other reactions have been proposed, such as the disproportionation of SO_2^{+} into SO and SO_3^{2-} [5,9–11], but these hypotheses have not been confirmed. The second oxidation peak observed on the voltammograms (Fig. 1) has been assigned to the oxidation of S_2O_4^{2-} [5,11,12], S_2O_4^{2-} [4,7], S_3O_6^{2-} [11], or SO_3^{2-} [9,10], and obviously its interpretation needs to be clarified.

The experimental results also depend on the solvent, but only a few authors have studied its influence [10,17,18]. It seems that it modifies mainly the equilibrium constants of the reactions. Each study has linked these variations to a different parameter of the solvent: basicity [10], Gutmann donor number [17], dielectric constant [18].

The choice of the supporting electrolyte also has an influence, which is better understood than that of the solvent. The main parameter is the size of the cation of the salt: with small cations, the dithionite salt is much less soluble [19], and its precipitation leads to the observation of adsorption phenomena [8,10].

This shows that the mechanism of the electrochemical reduction of SO_2 in non-aqueous solvents is not well understood. Some of the reduced species have not been identified clearly, and the experimental results are not always coherent: for instance, between two and four oxidation peaks have been observed on the voltammograms of a SO_2 solution. Consequently, the assignment of these peaks is controversial, as well as that of the redox couples, and their redox potential. Moreover, there have been very few studies of the influence of the temperature, and of the potential scan rate; thus, the kinetic parameters are not well known.

In order to identify and characterize the reduced species, we have used an original approach: we have determined a way of obtaining these species in stable solutions, at equilibrium [20]. This is achieved by reducing SO_2 chemically by lithium, in solution in hexamethylphosphoramide (HMPA). This method leads to stable polythionite solutions, Li(SO_2)_n + HMPA, where the relative concentration of the reduced species is accurately controlled through the adjustment of n, the SO_2/Li ratio.

Our recent spectroscopic study of the polythionite solutions [21] led to the identification and characterization of the reduced species at equilibrium. SO_2^{+} and its dimer, S_2O_4^{2-}, were identified in totally reduced solutions, i.e. solutions with n = 1. For solutions with n > 1, S_2O_4^{2-} was observed by ESR spectroscopy, and a new species was identified by its visible absorption band: S_3O_6^{2-}, the dimer of S_2O_4^{2-}:

\[
2\text{S}_2\text{O}_4^{2-} \rightleftharpoons \text{S}_3\text{O}_6^{2-} \quad (6)
\]

It has been shown [21] that S_3O_6^{2-} is the blue complex, previously identified as S_2O_4^{2-}. Upon addition of a supporting electrolyte (with a large cation), the red complex S_2O_6^{2-} was observed, and it was shown, from spectroelectrochemical experiments [21], that this species is formed by reaction between SO_2^{+} and S_2O_4^{2-} (Eq. (4)). The spectroscopic study of the polythionite solutions allowed the chemical reactions between the species resulting from the reduction of SO_2 to be identified. This is an important point, because these are the same reactions which are coupled to the electron transfers occurring in the electrochemical reduction of SO_2. Moreover, the quantitative analysis of the experimental results led to the determination of the equilibrium constants of these reactions, which is very useful for the analysis of the electrochemistry experiments.

A preliminary electrochemical study of the polythionite solutions was performed [22]. The study of polythionite solutions with n = 1 showed that the dithionite anion, S_2O_4^{2-}, is not electroactive, which had never been considered before. For all polythionite solutions with n > 1, and for SO_2 solutions, a prewave is observed in addition to the main reduction peak. This prewave was shown to be the reduction of S_2O_4, the dimer of SO_2 [23]:

Fig. 1. Cyclic voltammogram of a 4.4 mM SO_2 + DMSO solution. Working electrode: Pt, area 3.14 mm^2. Scan rate: 200 mV s^{-1}. 

2SO₂ ⇔ S₂O₄  
S₂O₄ + e⁻ ⇔ S₂O₄⁻  

(7)  
(8)  

This new species, S₂O₄, was identified in SO₂ solutions and characterized by spectrophotometry [23]. We have observed that the first oxidation peak splits into two peaks at low scan rates, and these two peaks are associated with the two reduction peaks. The two redox couples involved were shown to be SO₂/SO₂⁻ and S₂O₄/S₂O₄⁻ [22].

However, a number of questions remain open about the interpretation of the voltammograms. For instance, some species have been shown to be electroactive (SO₂, S₂O₄⁻, SO₂⁻ and S₂O₄⁻), and the dithionite, not to be electroactive, but two species, S₂O₄⁻ and S₂O₄²⁻, were identified during the spectroscopic study of the polythionite solutions, and their electrochemical behavior is unknown.

We present in this paper the detailed electrochemical study of sulfur dioxide solutions in HMPA. The analysis of the experimental results allows us to build a global mechanism to explain the reduction of SO₂, taking into account all the peaks observed on the voltammograms. For the first time, this mechanism is simulated and adjusted to the experimental data, and the values obtained for the parameters are discussed. This model brings an answer to the remaining questions listed above. Finally, it is proved to be valid in other non-aqueous solvents.

2. Experimental

2.1. Materials

The choice of hexamethylphosphoramide (HMPA) as a solvent has been discussed elsewhere [20]. HMPA (Aldrich, 99%) was dried on NaH for at least 24 h, then distilled twice at 100°C [24]. SO₂ (L’Air Liquide, > 99.7%) was purified on H₂SO₄, then on P₂O₅ [25]. Lithium (Fluka, 99%) was used as received. Tetraethylammonium perchlorate (TEAP, Fluka, > 99%) was dried under vacuum at 150°C for at least 24 h. It was used as the supporting electrolyte at a concentration of 0.1 mol dm⁻³. All solutions were prepared and stored in a glove box with a dry oxygen-free argon atmosphere. In order to minimize losses of SO₂, the volume of the gas phase relative to the volume of the liquid phase was kept as small as possible.

2.2. Apparatus

Cyclic voltammetric experiments were carried out at 20 ± 0.1°C with a BAS 100 B electrochemical analyzer, in a three-electrode cell. The working electrode was a 2 mm-diameter platinum disk, polished to a mirror finish. Platinum wires were used as auxiliary and pseudo-reference electrodes. The ferricinium/ferrocene (Fc⁺/Fc) couple was used as an internal potential reference. An ohmic drop compensation was applied when necessary.

All voltammograms shown in this paper are plotted according to the IUPAC convention (negative reduction currents), and the voltammograms have been normalized to the square root of the potential scan rate. This representation allows us to show the differences from a simple, infinitely fast electron-transfer mechanism.

The experimental setup for the spectroelectrochemistry experiments has been described previously [26]. The cell used can be operated either under semi-infinite diffusion or under thin layer conditions. Under these conditions, the solution layer was between 100 and 200 μm thick. From the electrochemical point of view, it is a classical three-electrode cell. The working electrode was a 5 mm-diameter platinum disk, polished to a mirror finish.

3. Results and discussion

3.1. Voltammetric study of SO₂ + HMPA solutions

SO₂ + HMPA solutions were studied at various concentrations and potential scan rates. The influence of the temperature could not be examined, because the available temperature range is too low: the melting point of HMPA is 7°C, and excessive heating results in losses of sulfur dioxide [27]. However, studies at various temperatures were made in DMF, down to −60°C. These results are mentioned below (Section 3.4).

A typical voltammogram obtained for a SO₂ + HMPA solution in semi-infinite diffusion conditions is displayed on Fig. 2. In addition to the main reduction peak (R₁), a prewave (R₂) is observed, at a slightly higher potential. One more shoulder (R₃) is observed in some experiments, at a lower potential. In the reverse scan, three oxidation peaks are present (O₁, O₂ and O₃). O₁ and O₂ are located at very close potentials, and are not always well resolved. The third peak, O₃, has no reversibility, whatever the experimental conditions. Moreover, O₃ is not observed for an initial positive scan. It is therefore the consequence of the potential scan through R₁, R₂, R₃, O₁ and O₂. This shows that the species oxidized on O₁ is not present in solution at equilibrium, but is formed during the first part of the experiment.

The potential scan rate has little influence on R₁ (Fig. 3), but R₂ is favored at low scan rates, which is an indication of a CE mechanism: a chemical equation is coupled to the electron transfer, leading to the formation of a species that is reduced at this potential. R₁ is
Fig. 2. Cyclic voltammogram of a 9.8 mM SO₂⁻ + HMPA solution. Working electrode: Pt, area 3.14 mm². Scan rate: 200 mV s⁻¹.

Fig. 3. Experimental cyclic voltammograms of a 9.8 mM SO₂⁻ + HMPA solution. The experiments were run for scan rates of 5000, 2000, 1000, 500, 200, 100 and 50 mV s⁻¹. Indicates the variation of the normalized current with increasing scan rates. Scan rates shown here: (+) 2000 mV s⁻¹; (——) 500 mV s⁻¹; (—) 100 mV s⁻¹. Working electrode: Pt, area 3.14 mm².

observed only for scan rates between 100 and 500 mV s⁻¹. O₁ and O₂ are favored at low scan rates (Fig. 3), and they are also better resolved under these conditions. The normalized intensity of O₃ displays only small changes for the scan rates displayed here, but O₃ disappears at very low scan rates (v < 5 mV s⁻¹), and increases at high scan rates (v > 20 V s⁻¹).

The influence of the concentration of SO₂⁻ has been studied previously [23]. The available range is limited because we have observed adsorption phenomena for concentrations above 10 mM. The prewave R₂ increases relative to R₁ when the concentration increases, and the shoulder R₁' is observed only when the concentration is above 5 mM. Increasing the concentration has little effect on the normalized current of O₁ and O₂. O₃ is slightly more intense at high concentration, and its potential is strongly shifted: it is decreased by about 300 mV when the concentration is increased from 2 to 10 mM.

3.2. Elaboration of a complete reduction mechanism

The electrochemical study of polythionite solutions [22] has led to a partial mechanism, explaining R₁, R₂, O₁ and O₂:

\[
SO₂⁻ + e⁻ ⇌ SO₂⁻\,
\]

\[
2SO₂ ⇌ S₂O₄²⁻
\]

\[
S₄O₄²⁻ + e⁻ ⇌ S₄O₄⁻²
\]

\[
SO₂⁺ + SO₂⁻ ⇌ S₂O₄⁻²
\]

It was shown that two redox couples are present: SO₂⁻/SO₂⁻ (R₁, O₁) and S₂O₄²⁻/S₄O₄⁻² (R₂, O₂). The R₂ peak is favored relative to R₁ when the concentration increases, because of the dimerization equilibrium of SO₂⁻ (Eq. (7)): the concentration of S₂O₄ at equilibrium increases relative to that of SO₂⁻. The existence of this equilibrium explains that R₂ is better observed at low scan rates: the dimerization equilibrium is fast enough to replace S₂O₄ progressively as it is reduced.

This set of reactions can also explain the R₁' shoulder: S₄O₄⁻², formed on R₂, can dissociate into SO₂⁻ and SO₂⁺ (Eq. (3)). This reaction leads to the formation of SO₂⁻, which is reduced on R₁. If the dissociation of S₄O₄⁻² is slow, SO₂⁻ will be formed at a potential lower than that of R₁, and will be reduced immediately, giving the R₁' shoulder. At low scan rates, R₁' is not observed, because SO₂⁻ is formed and reduced on R₁, and at high scan rates, S₄O₄⁻² has not enough time to dissociate, and R₁' is not observed either. Moreover, R₁' appears only at high concentration, because its intensity depends on the amount of S₂O₄⁻² formed, which depends in turn on the amount of S₄O₄⁻² present at equilibrium. The numerical adjustment of the voltammograms (see below) will show that this hypothesis can be accepted, because the R₁' shoulder appears without adding any equation to the model.

The O₃ peak is not observed at low scan rates (v < 5 mV s⁻¹), and it increases for high scan rates. It is then the oxidation of a species consumed on O₁, O₂; at high scan rates, this species is only weakly consumed, and at very low scan rates, this species has fully disappeared before the potential of O₃ is reached. Consequently, we interpret O₃ as the oxidation of the red complex S₄O₆⁻²:

\[
S₄O₆⁻² ⇌ S₄O₄⁻² + e⁻
\]
sumed on \( O_1 \) and \( O_2 \) through the oxidation of \( S_2O_4^\cdot \) and \( SO_2^\cdot \). In previous work, only Knittel [11] had considered that \( S_2O_6^2^- \) could be electroactive. This interpretation also explains the potential shift of \( O_3 \) with the scan rate: this variation is expected from the work of Andrieux et al. [28,29]. \( O_3 \) is never reversible, even at very high scan rates, because the oxidation of \( S_2O_6^2^- \) leads to \( S_2O_4^\cdot \). During the spectroscopic study of polythionite solutions, it was shown that \( S_2O_6^2^- \) is not stable in solution at equilibrium. \( S_2O_6^2^- \), produced at the electrode, dissociates quickly, through one of the following reactions:

\[
S_2O_6^2^- = SO_2 + S_2O_4^\cdot \tag{10}
\]

\[
S_2O_6^2^- = SO_2^\cdot + S_2O_4 \tag{11}
\]

In both cases, one of the species formed is oxidized at the potential of \( O_1; SO_2^\cdot \) or \( S_2O_4^\cdot \). The simulation and adjustments of the voltammograms will show that this interpretation is satisfactory.

### 3.3. Simulation and adjustment

The mechanism of the reduction of \( SO_2 \) is summarized in Scheme 1. It is composed of three electron transfers, and a set of coupled chemical reactions. This mechanism has been simulated and fitted to all the experimental voltammograms. This calculation has been performed with the Digisim® 2.1 software (BAS) [30]. For this adjustment, the voltammograms obtained for the six scan rates investigated, at a given temperature, were fitted simultaneously. The fitted parameters are \( E^0, \alpha \) and \( k^0 \) for each electron transfer reaction, and the equilibrium constants \( (K_{eq}) \) and forward rate constants \( (k_f) \) for the homogeneous reactions. It was assumed that the diffusion coefficients of all species were identical, and an average diffusion coefficient \( D \) was used, in order to avoid any divergent calculation during the adjustment.

A spectroscopic study of the polythionite solutions gives the values of the equilibrium constants in the absence of a supporting electrolyte [21]. The red complex was observed only in the presence of a supporting electrolyte, but an estimation of the equilibrium constant of its formation could be given [21]. These equilibrium constants were very helpful for the adjustment calculations, as they were used as initial values.

Fig. 4 displays the voltammograms simulated at various scan rates, with the final parameters obtained by the adjustment process. They are to be compared with the experimental voltammograms displayed in Fig. 3. The similarity of the reduction peaks is excellent; in particular, the shoulder \( R_1 \) is present, which confirms that it was not necessary to add another electron transfer reaction to the model. The agreement is not so good for the oxidation peaks, because some weak adsorption occurs in the potential range of \( O_1 \) and \( O_2 \), and because \( O_3 \) is not very marked: the residual current disturbs the adjustment calculation.

The parameters obtained for these three electron transfer reactions are given in Table 1. The \( \alpha \) coefficient for the oxidation of \( S_2O_6^2^- \) was set equal to 0.5 and was not allowed to vary, because the \( O_3 \) peak is weak and not reversible, which does not allow the fitting calculation to converge towards a well-defined value. For the other two reactions, the \( \alpha \) values are not very different from 0.5. The electron transfer rate constants are in the same range for the three reactions, and they are characteristic of quasi-reversible electron transfers. These values cannot be compared to literature data, because these parameters had never been determined before.

---

**Scheme 1. Mechanism of the reduction of \( SO_2 \).**

**Fig. 4.** Cyclic voltammograms of a 9.8 mM \( SO_2 \) + HMPA solution, calculated by using the parameters obtained from the adjustment calculations. The adjustment was performed for the voltammograms at the seven scan rates investigated (5000, 2000, 1000, 500, 200, 100 and 50 mV s\(^{-1}\)). Indicates the variation of the normalized current with increasing scan rates. Scan rates shown here: (+) 2000 mV s\(^{-1}\); (— — —) 500 mV s\(^{-1}\), (—) 100 mV s\(^{-1}\). These voltammograms are to be compared to the experimental voltammograms (Fig. 3)
The formation of the red complex by reaction between SO₂ and S₃O₆⁻ (Eq. (5)) is very fast in both the forward and backward directions. This explains why this reaction has no influence on the voltammograms, at the potential scan rates investigated. This confirms the conclusions of the spectroelectrochemical study of polythionite solutions [21], which showed that, in the course of a voltammetric experiment, S₃O₆⁻ was formed mainly by reaction between SO₂⁻ and S₂O₄²⁻ (Eq. (4)). The equilibrium constant for this reaction, \( K_\text{d} \), is close to the estimation of 625 M⁻¹ which has been made previously [21].

The values obtained for the equilibrium constants are of the same order of magnitude as those obtained in the previous studies, which were done in other solvents. However, making a direct comparison is impossible, because the previous models were different: for instance, these studies did not consider the dimerization of S₃O₄²⁻.

The equilibrium constants obtained by the adjustment of the voltammograms can be compared to those measured during the spectroscopic study of the polythionite solutions (Table 3) [21]. The values are different, because polythionite solutions were studied in the

### Table 2
Parameters of the homogeneous chemical reactions, obtained from the same calculation as in Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( K_{\text{eq}}/\text{M}^{-1} )</th>
<th>( k / \text{s}^{-1} )</th>
<th>( k = (k_{\text{eq}}/K_{\text{eq}}) / \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2SO₂ ( \rightleftharpoons ) S₂O₄⁻</td>
<td>26 ± 6</td>
<td>3000</td>
<td>110</td>
</tr>
<tr>
<td>2SO₂⁻ ( \rightleftharpoons ) S₂O₄²⁻</td>
<td>5530 ± 1700</td>
<td>1350</td>
<td>0.25</td>
</tr>
<tr>
<td>2S₂O₄²⁻ ( \rightleftharpoons ) S₃O₆⁻</td>
<td>220 ± 97</td>
<td>25</td>
<td>0.11</td>
</tr>
<tr>
<td>SO₂ + S₂O₄²⁻ ( \rightleftharpoons ) S₃O₆⁻</td>
<td>2780 ± 280</td>
<td>( 10^8 ) a</td>
<td>3.6 ( \times ) ( 10^4 )</td>
</tr>
<tr>
<td>S₂O₄⁻ + SO₂⁻ ( \rightleftharpoons ) S₃O₆⁻</td>
<td>2220 ± 960</td>
<td>( 2 \times 10^4 ) a</td>
<td>10</td>
</tr>
<tr>
<td>S₃O₆⁻ ( \rightleftharpoons ) SO₂ + S₂O₄²⁻</td>
<td>( 10^8 ) a</td>
<td>( 10^8 ) a</td>
<td>1</td>
</tr>
</tbody>
</table>

\( a \) Constant values.

---

Table 2 displays the values obtained for the equilibrium constants and rate constants of the homogeneous reactions: some values have been imposed and the others have been determined from the adjustment procedure. The oxidation of S₃O₂⁻ is essentially a first-order EC reaction, the dissociation of S₃O₆⁻ \( \ast \) (Eq. (10)) being the follow-up reaction involved. As the O₁ peak is irreversible, the values of the rate constant of reaction 10 and \( E_{\text{f}} \) cannot be evaluated independently [31]. The values of these parameters are coupled so that there is an infinite number of parameter values that will produce virtually identical simulations. In order to obtain an irreversible wave, the reaction rate has been taken arbitrarily constant and equal to \( 10^8 \) s⁻¹. The equilibrium constant of reaction 10 was also set equal to \( 10^8 \) M⁻¹. Furthermore, after several iterations in the adjustment procedure, it was clear that the rate constant \( k_1 \) of Eq. (5) was very high, and consequently its value was set equal to \( 10^8 \) s⁻¹.

The dimerization rate constant of SO₂⁻ \( \ast \) is only moderately high, while the electrochemical study of the polythionite solutions had led us to conclude qualitatively that this reaction was fast [22]. Moreover, the equilibrium constant of this reaction (Eq. (2)), deduced from the adjustment of the voltammograms (Table 2), is ten times smaller than the value determined in the absence of a supporting electrolyte. This is in opposition with the variation expected from the increase of the ionic strength [32]: equilibria involving charged species are shifted towards the dimer species when the ionic strength is increased. The too low value for \( K_{\text{d}} \) (SO₂⁻ \( \ast \)) leads to an overestimation of the concentration of SO₂⁻ \( \ast \), which results in an increase of the intensity of O₁. This can be related to the small adsorption phenomenon observed at this potential: the diffusion current is smaller than the effectively measured current. As the simulation program takes into account only diffusion processes, it leads to an overestimation of the concentration of SO₂⁻ \( \ast \), in order to increase the intensity of O₁. The species involved in this adsorption phenomenon is very probably the dithionite, as was already observed in previous studies [8,10].
Table 3
Comparison of the equilibrium constants of the chemical reactions, in the presence of TEAP or not.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K_{eq}$ without TEAP/M$^{-1}$</th>
<th>$K_{eq}$ with TEAP/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{SO}_2 \rightleftharpoons \text{S}_2\text{O}_4$</td>
<td>77 ± 25</td>
<td>26 ± 6</td>
</tr>
<tr>
<td>$2\text{SO}_2^- \rightleftharpoons \text{S}_2\text{O}_4^{2-}$</td>
<td>$(66 \pm 2.0) \times 10^4$</td>
<td>5530 ± 1700</td>
</tr>
<tr>
<td>$2\text{SO}_2^- \rightleftharpoons \text{S}_2\text{O}_4^{2-}$</td>
<td>130 ± 50</td>
<td>220 ± 100</td>
</tr>
<tr>
<td>$\text{SO}_2 + \text{SO}_2^- \rightleftharpoons \text{S}_2\text{O}_4^{2-}$</td>
<td>2000 ± 600</td>
<td>6900 ± 2000</td>
</tr>
</tbody>
</table>

*The values in the absence of TEAP were determined from the spectroscopic study of polythionite solutions [21]; the values in the presence of TEAP are obtained from the numerical adjustment of the voltammograms.

absence of a supporting electrolyte. The formation of the red complex is not mentioned here, because this species is observed only when a supporting electrolyte is added [32].

The presence of a supporting electrolyte leads to an increase of the ionic strength, which modifies the apparent value of the equilibrium constants. Equilibria involving neutral species are shifted towards the dissociation of species, while for charged species the complexation is favored [32].

The value of $K_{\text{dim.}} (\text{SO}_2)$ is smaller in the presence of TEAP, which was expected because both SO$_2$ and S$_2$O$_4$ are neutral species. For all other reactions, except the dimerization of SO$_2^-$, the equilibrium constant increases, as expected.

This analysis shows that the values of the equilibrium constants obtained here from the electrochemical study are coherent with those measured during the spectroscopic study of polythionite solutions. An exception is the case of the dimerization of SO$_2^-$, which has been discussed above.

These parameters have been obtained from the adjustment of the voltammograms of SO$_2$ + HMPA solutions, recorded under semi-infinite diffusion conditions. By using these parameters, we have simulated (without any adjustment) voltammograms of polythionite solutions, and of SO$_2$ solutions in thin layer conditions. To be acceptable, the same set of parameters must also explain these experimental results.

Under thin layer conditions (Fig. 5), the simulated and experimental voltammograms are in good agreement: the $R_1$, $R_2$, $O_1$ and $O_2$ peaks are well resolved and their intensity is similar. In that case, the simulation is performed very easily, by changing one of the options of the Digisim® 2.1 software.

Simulating the voltammogram of a polythionite solution is more difficult: it is then necessary to change the equilibrium potential of the solution, because the equilibrium potential of such a solution is obviously different from that of a SO$_2$ solution. For the simulation, it is not possible to describe the composition of the solution by using the only two parameters we know: $n$ and [Li$^+$]. The only possibility is to change the initial potential of the experiment, in order to make it coincide with the equilibrium potential of the solution. This method does not allow us to monitor the reduction degree of the solution (the value of $n$). However, if the initial potential is chosen carefully, the simulated voltammograms are in good agreement with the experimental results (Fig. 6). The distortion of the experimental voltammograms displayed here is due to non-faradaic current, because the measured intensity is

Fig. 5. Experimental and simulated cyclic voltammograms of a 9.8 mM SO$_2$ + HMPA solution, under thin layer conditions (f = 100 µm). Scan rate: 5 mV s$^{-1}$. The simulation is performed with the parameters obtained from the adjustment calculations.
Fig. 6. Experimental and simulated cyclic voltammograms of a polythionite solution. Scan rate: 1 V s⁻¹. Experimental voltammograms: polythionite solution Li(SO₂)₆ HMPA with \(n = 1.5\) and \([\text{Li}^+] = 5 \text{ mM}\), working electrode: Pt, area 3.14 mm². The simulation is performed with the parameters obtained from the adjustment calculations, and by changing the initial potential of the experiment.

weak. This method is applied successfully for any value of \(n\).

Another point to be checked is that this set of parameters (Tables 1 and 2) is coherent with the results of the spectroscopic study of the polythionite solutions [21]. Knowing the values of all equilibrium constants in the model (Table 2), we can calculate the concentration of every species in a given polythionite solution [21]. Then, these values are compared to the absorbance of the bands of each species, deduced from the decomposition of the UV–vis spectra. Fig. 7 displays this comparison for the 498 nm absorption band, assigned to \(\text{S}_4\text{O}_6^{2-}\), and for the 595.7 nm absorption band, assigned to \(\text{S}_2\text{O}_6^{2-}\). In each case, the variations with \(n\) for \([\text{Li}^+] = 5 \text{ mM}\) are similar for the calculated concentration and for the measured absorbance. The good agreement between these two independent sets of data indicates that the model we have built, and its parameters, are valid.

For the 498 nm absorption band, the comparison between the absorbance and the concentration of \(\text{S}_4\text{O}_6^{2-}\) (Fig. 7(b)) also allows us to determine the extinction coefficient, which could not be done previously [21]. We obtain \(\varepsilon(\text{S}_4\text{O}_6^{2-}, 498 \text{ nm}) = 2670 \text{ M}^{-1} \text{ cm}^{-1}\).

3.4. Study in other non-aqueous solvents

The choice of HMPA as a solvent has been imposed by the method used to prepare the polythionite solutions, because the solvent used had to be inert towards lithium [20]. This limitation does not apply for \(\text{SO}_2\) solutions, and \(\text{SO}_2\) is soluble in a number of non-aqueous solvents [33]. Therefore, we have also performed an electrochemical study of \(\text{SO}_2\) solutions in DMF, DMSO and acetonitrile.

For \(\text{SO}_2\) solutions in DMSO and DMF (Fig. 8), the voltammograms are very similar to those observed in HMPA, and to those shown in the previous studies [4–13]. In acetonitrile, some adsorption occurs, which results in distorted and poorly reproducible voltammograms.

The strong similarity between the observations in various non-aqueous solvents allows us to conclude that the reduction mechanism must not be very different from the model built in the case of HMPA. However, the resolution of the peaks is better in HMPA, especially for the prewave \(R_2\), and the intensity of the \(O_3\) peak is different. This means that the equilibrium constants are somewhat different from one solvent to another. For this reason, adjustment of the voltammograms could not be reached easily, because no initial values are available, contrary to the case of HMPA.

One advantage of DMF is its low melting point, which allowed us to study \(\text{SO}_2\) solutions down to \(-60^\circ\text{C}\). In DMF, the prewave \(R_1\) is weak at \(20^\circ\text{C}\), but its intensity increases strongly when the temperature increases: the rate constants of the preceding reaction, the dimerization of \(\text{SO}_2\), are increased. For temperatures lower than \(20^\circ\text{C}\), \(R_2\) is not observed. This means either that the potentials of the two redox couples are closer to each other than in HMPA, or that the dimerization of \(\text{SO}_2\) is stronger in HMPA than in DMF. The oxidation peaks \(O_1\) and \(O_2\) are also less intense when the temperature decreases: the dimerization reactions are shifted towards the dimer species, \(\text{S}_2\text{O}_4^{2-}\) and \(\text{S}_4\text{O}_8^{2-}\), and the concentration of the electroactive species, \(\text{SO}_2^{2-}\) and \(\text{S}_2\text{O}_4^{2-}\), is decreased.

Spectroelectrochemistry experiments have also been done in DMF: this solvent allows the study of more concentrated \(\text{SO}_2\) solutions than in HMPA, because no adsorption is observed, and because the supporting electrolyte used, TEAP, is more soluble. The experi-
mental observations are then easier, because the absorbances measured are higher. The results are very similar to those obtained in HMPA, which confirms that the reduction mechanism of SO$_2$ is the same in these two solvents.

3.5. Discussion

We can now conclude that the proposed mechanism (Scheme 1) describes accurately the reduction of SO$_2$ in non-aqueous solvents. The values of the parameters obtained from the adjustment of the voltammograms are coherent with those obtained from the spectroscopic study of the polythionite solutions [21]. Moreover, this model explains the electrochemical observations for all types of solutions (reduced or not), and both under semi-infinite diffusion and thin layer conditions. Most of the study was done in the case of HMPA, but it has been shown that this mechanism is also valid in other non-aqueous solvents, such as DMF or DMSO.

Compared to the previous studies, two new reactions have been introduced: the dimerization of SO$_2$, and that of S$_2$O$_4^{2-}$. All the other reactions have already been mentioned, but not always simultaneously in a given model. On the other hand, we have no indication of a disproportionation of SO$_2^{2-}$, a reaction which had been proposed by several authors, but whose products have never been observed [5,9–11].

From the electrochemical point of view, the non-electroactivity of S$_2$O$_4^{2-}$ had never been envisaged before, but only the study of strongly reduced solutions could lead to this conclusion. Finally, the O$_3$ peak is explained as the oxidation of S$_3$O$_6^{2-}$ into S$_3$O$_6^{2-}$, which dissociates immediately.

The observation that the red complex S$_3$O$_6^{2-}$ is stable confirms the non-existence of the redox couple S$_2$O$_4^{2-}$ / S$_3$O$_6^{2-}$. The impossibility of an electron transfer between these two species could be explained by a different geometry: the Franck–Condon principle states that the electron transfers occur at a much shorter time scale than displacements of the atoms; in other words, the molecular configuration does not change during the electron transfer. The structure of S$_2$O$_4^{2-}$ in solution in non-aqueous solvents is known from X-ray diffraction and Raman spectroscopy measurements [19,34]: this molecule is composed of two SO$_2^{2-}$ units linked by a S–S bond (Scheme 2(a)). The structure of S$_2$O$_4^{2-}$ is more controversial, but ab initio calculations [35–37] indicate that SO$_2$ and SO$_2^{2-}$ are linked by a S–O or O–O bond (Scheme 2(b)). These structural differences explain the impossibility of any electron transfer. This analysis shows that our model is coherent: the stability or instability of the species is related to the existence or not of the redox couples, and to the structure of the species.

About the redox couple S$_3$O$_6^{2-}$ / S$_3$O$_6^{2-}$, we have shown that one of the species, S$_3$O$_6^{2-}$, is not stable in solution, while the other one, S$_3$O$_6^{2-}$, is [21]. The instability of S$_3$O$_6^{2-}$ is not due to its radical nature, since SO$_2^{2-}$ and S$_2$O$_4^{2-}$, which are also radicals, have been shown to be stable. Each of these two species, S$_3$O$_6^{2-}$ and S$_3$O$_6^{2-}$, can be formed through two reactions:

\[
\begin{align*}
SO_2 + S_2O_4^{2-} &\rightleftharpoons S_3O_6^{2-} \rightleftharpoons SO_2^{2-} + S_2O_4 \quad (12) \\
SO_2 + S_2O_4^{2-} &\rightleftharpoons S_3O_6^{2-} \rightleftharpoons S_2O_4^{2-} + SO_2^{2-} \quad (13)
\end{align*}
\]

The difference between the two sets of reactions is the existence, or not, of the corresponding redox couples. In the case of S$_3$O$_6^{2-}$, Eq. (12) results from the sum of the two electron transfers, those of the redox couples.

![Fig. 7. Absorbance (●, left axis scale) of the 595.7 nm band and of the 498 nm band, obtained by the decomposition of the UV–vis spectra of Li(SO$_2$)$_n$ + TEAP + HMPA solutions with [Li$^+$] = 5 mM and [TEAP] = 0.1 M, versus n [21]. For each value of n, at least three solutions were investigated, but only the mean value is plotted. The error bars take into account both the standard deviation of these measurements, and the error of the decomposition calculation. The 595.7 nm band is assigned to S$_4$O$_8^{2-}$, and the 498 nm band, to S$_3$O$_6^{2-}$. The concentration of these species (–, right axis scale) is calculated by using the mechanism and the equilibrium constants obtained from the adjustment of the voltammograms. For each species, the concentration follows the same variations as the absorbance. The comparison between the scales of the two ordinate axes allows us to determine the molar extinction coefficient of the absorption bands [21].]
SO$_2$/SO$_2^-$ Therefore, no intermediate species can exist in that case. On the contrary, for S$_3$O$_5^{2-}$, one of the species involved in Eq. (13), S$_2$O$_4^{2-}$, is not electroactive. The intermediate species, S$_3$O$_5^{2-}$, can then be stable in solution.

4. Conclusions

This study has led us to propose and to discuss a mechanism describing the electrochemical reduction of SO$_2$ in non-aqueous solvents (Scheme 1). For the building of this model, the results of the study of polythionite solutions have been very helpful; this study has given indications about the identification of the species, their electroactivity, and an estimation of the equilibrium constants of the homogeneous reactions. This model allows us to explain the experimental observations for SO$_2$ solutions and for polythionite solutions, both in semi-infinite diffusion and under thin layer conditions. It also describes the composition of the polythionite solutions for any value of $n$ and [Li$^+$].

The small value of the oxidation currents, which had always been a major difficulty for the interpretation in the previous studies, is now explained: the oxidizable species, SO$_2^-$, S$_2$O$_4^{-}$ and S$_3$O$_5^{2-}$, are always present at low concentration, because of the existence of the dimer species S$_2$O$_4^{2-}$ and S$_4$O$_8^{2-}$.

It would be also interesting to see if a relation can be established between the structure of the species and their electroactivity: S$_3$O$_5^{2-}$ is electroactive, while S$_2$O$_4^{2-}$ is not, and we have no indication for the electroactivity of S$_4$O$_8^{2-}$. This could be due to a difference in the structure of these species, but only for S$_3$O$_5^{2-}$ has the structure been investigated in the literature [19,34].

However, the reduction mechanism of SO$_2$ in non-aqueous solvents is now well understood. This will be very useful for the optimization of the various applications involving reduced SO$_2$. Moreover, the idea of studying chemically reduced solutions (the polythionite solutions) has proved to be very useful, and a similar procedure could be of great help in understanding other reduction mechanisms.

Acknowledgements

The authors are grateful to Dr F.-X. Sauvage for a critical reading of the manuscript. One of the authors (EP) wishes to thank the “Ministère de l’Education Nationale et de l’Enseignement Supérieur et de la Recherche” for granting her a doctoral scholarship.
References