

# The Determination of Thermodynamic and Heterogeneous Kinetic Parameters of the TMPD/TMPD<sup>•+</sup> Redox Couple in Tetrahydrofurane and n-Butanol Using Ultramicroelectrodes. Quasi Steady-State Voltammetry

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Relata-se a determinação dos parâmetros termodinâmicos e cinéticos da oxidação monoelétrica de N,N,N',N'-tetrametil p-fenilendiamina (TMPD) para seu monocátion radical correspondente (TMPD<sup>•+</sup>) sobre ultramicroeletrodos de discos de platina de diferentes raios em meios altamente resistentes. As cinéticas são estudadas por voltametria de estado quase estacionário usando-se tetrahydrofurano e n-butanol como solventes. Um procedimento recentemente desenvolvido por Galus *et al.* foi usado para realizar estes estudos voltamétricos. Os resultados obtidos em tetrahydrofurano são comparados com aqueles obtidos para o mesmo par redox usando eletrodos de tamanho convencional. A comparação destes novos resultados obtidos em meio de n-butanol foi impossível de ser feita devido à falta de informações de literatura.

The determination of thermodynamic and kinetic parameters for one-electron oxidation of N,N,N',N'-tetramethyl p-phenylendiamine (TMPD) to its corresponding monocation radical (TMPD<sup>•+</sup>) on platinum disk ultramicroelectrodes of different radii in highly resistive media is discussed. The kinetics are studied using tetrahydrofurane and n-butanol as solvents and employing quasi steady-state voltammetry. A procedure recently developed by Galus *et al.* was used to carry out these voltammetric studies. The results obtained for tetrahydrofurane are compared with those determined for the same redox couple using conventional size electrodes. The comparison of these new results obtained in the n-butanol medium was impossible due to the lack of information in the literature.

**Keywords:** *thermodynamic parameters, kinetic parameters, ultramicroelectrodes*

## Introduction

The use of ultramicroelectrodes (UME) has led to a renewed interest in quasi steady-state voltammetry (QSSV), since the use of UME enables the extraction of heterogeneous electron-transfer kinetic parameters, *i.e.* the formal rate constant ( $k_f^0$ ) and transfer coefficient ( $1 - \alpha$ ) of electrochemical reactions using quick and simple methods<sup>1-7</sup>. Most of these methods, developed for an inlaid microdisk, require data obtained from electrodes of different radii ( $r$ )<sup>3-5</sup>, and for quasi-reversible systems an independent determination of the formal potential ( $E_f^0$ ) is necessary<sup>2,3,5</sup>. However, in some cases, the above mentioned parameters can be derived from a single quasi steady-state (QSS) voltammogram, assuming that the  $r$  of the UME and the diffusion coefficient of the reactant ( $D_R$ )<sup>3,6</sup> are known.

The most important advantages of QSSV over the relaxation methods, such as cyclic voltammetry (CV) include the absence of the limitations caused by the charging current and ohmic polarization, which often interfere in transient techniques<sup>8</sup>. Thus, QSSV on UME could be used to obtain the thermodynamic and kinetic parameters in high resistive media. This is very difficult and sometimes impossible through the use of traditional techniques on conventional size electrodes (CSE) or by transient techniques on UME<sup>9</sup>.

In recent years, we have been studying the solvent effect on  $k_f^0$ ,  $(1 - \alpha)$  and  $(E_f^0)$  for the oxidation of N,N,N',N'-tetramethyl p-phenylendiamine (TMPD) on platinum CSE<sup>10</sup>. Thus, electrochemical measurements in relatively high resistive media [*i.e.* tetrahydrofurane (THF) as solvent] could be

only performed at a concentration of the supporting electrolyte ( $\text{NaClO}_4$ ) as high as  $0.8 \text{ M}^{10}$ . However, not a single value for the electrochemical parameters could be obtained in another resistive solvent such as *n*-butanol (*n*-BuOH) when using CSE, mainly due to conductivity limitations derived from supporting electrolyte solubility restrictions.

In this work, the oxidation of TMPD to its corresponding radical cation ( $\text{TMPD}^{\bullet+}$ ) on platinum UME of different  $r$  is studied in THF and *n*-BuOH by QSSV using  $0.1 \text{ M}$  and  $0.3 \text{ M}$   $\text{NaClO}_4$  and  $0.1 \text{ M}$   $(\text{C}_4\text{H}_9)_4\text{NClO}_4$  (TBAP), respectively, as the supporting electrolytes at  $293 \text{ K}$ . The kinetic parameters are mainly determined using the methodology proposed by Galus *et al.*<sup>3</sup>. In addition, the values obtained are compared with those calculated applying the method developed by Mirkin *et al.*<sup>6</sup>. The TMPD/ $\text{TMPD}^{\bullet+}$  couple was chosen as the electrochemical system because it is well known that it conforms to a simple one-electron reversible process<sup>11-13</sup>. The method of calculus of the kinetic parameters is based on the application of either of the following equations<sup>3</sup>:

$$\ln[(i_L - i)/i - (i_L - i_r)/i_r] = \ln(4D_R/\pi r k_f^0) - (1 - \alpha)nf(E - E_f^0) \quad (1)$$

or

$$i_L/i = 4D_R/\pi k_f r + i_L/i_r \quad (2)$$

where  $f = F/RT$ ,  $i_r$  is the calculated reversible current,  $i$  the measured current for the kinetically controlled process at potential  $E$ ,  $i_L$  the limiting current,  $k_f$  the forward rate constant, and the other terms have the usual meaning. The  $(i_L - i_r)/i_r$  term can be obtained if  $E_f^0 \cong E_{1/2}^0$  is known<sup>3,8,10</sup>. The  $(i_L - i)/i$  term is determined from the experimental QSS voltammograms. For a given  $r$ , a  $\ln[(i_L - i)/i - (i_L - i_r)/i_r]$  vs.  $(E - E_f^0)$  plot (Eq. 1) should be linear with a slope equal to  $(1 - \alpha)nf$  and an intercept equal to  $\ln(4D_R/\pi r k_f^0)$ . Assuming that  $n$ ,  $D_R$  and  $r$  are known,  $k_f^0$  and  $(1 - \alpha)$  can be obtained from the intercept and slope, respectively.

A plot of  $i_L/i$  vs.  $1/r$  (Eq. 2) should be linear, with a slope equal to  $4D_R/\pi k_f$ , from which  $k_f$  can be obtained for a given  $E$ . By extrapolating from  $1/r = 0$ , it is possible to determine  $i_L/i_r$ , which can be independently checked. Then  $k_f^0$  and  $(1 - \alpha)$  can be determined from the classical  $\ln k_f$  vs.  $E$  plots<sup>14</sup>.

## Experimental

THF (Sintorgan, HPLC) and *n*-BuOH (Sintorgan, HPLC) were dried over 3 and 4 Å molecular sieves respectively, for 48 h prior to use and were then used without further purification.  $\text{NaClO}_4$  (Koch Light A. R.) was purified as previously reported<sup>15</sup>. TBAP (Fluka, electrochemical grade) was dried under vacuum at  $60^\circ \text{C}$ .

TMPD was obtained from its dihydrochloride (Fluka A. G.) and purified as previously described<sup>13</sup>. The concentration of the reactant was in the range of  $0.1\text{--}7 \times 10^{-3} \text{ M}$ .

Electrochemical measurements were performed in a two-compartment Pyrex cell<sup>16</sup>. The working electrodes were platinum disk UMEs of different radii, constructed from platinum wires ( $r = 25 \mu\text{m}$ ) from Casa Eise S.A., as previously described<sup>17</sup>. Before each measurement, they were treated as explained elsewhere<sup>17,18</sup>. The radii of the largest UME,  $r_1$ , was determined from experimental data obtained from TMPD/acetonitrile/ $0.1 \text{ M}$   $\text{NaClO}_4$  solutions by a procedure previously described<sup>18</sup>. The radii of the other UMEs were calculated from the ratio of limiting currents of QSS voltammograms ( $i_{L,1}/i_{L,n} = r_1/r_n$ , where the subscripts 1 and  $n$  ( $n = 1, 2, 3, \dots$ ) indicate the largest and the other UME, respectively).

The counter electrode was a platinum foil with a large area (approx.  $2 \text{ cm}^2$ ). The reference electrode was an aqueous saturated calomel electrode (SCE) accommodated to the cell as previously reported<sup>16,19</sup>.

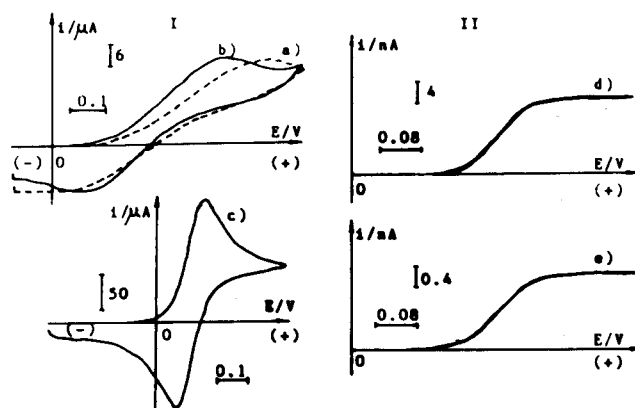
All solutions were de-aerated by bubbling pure nitrogen.

The  $D_R$  of TMPD was calculated through  $i_L$  values from QSS voltammograms, with the assumption that  $n$ ,  $r$  and  $C^*R$  are known.

The measuring system for QSSV and CV was constructed from an EG&G PARC 273 potentiostat and a Hewlett Packard Model 7035B recorder. The sweep rate,  $v$ , was in the range of  $0.005$  to  $0.050 \text{ V s}^{-1}$ . The  $i$ - $t$  transients were obtained from the same potentiostat and recorded on a REC 61 SERVOGRAPH recorder.

## Results and Discussion

Cyclic voltammograms for the TMPD/THF/ $\text{NaClO}_4$  system obtained with both platinum CSE (I) and UME (II) are shown in Fig. 1. The marked ohmic effect observed with the CSE is evident. Curve Ia corresponds to a cyclic vol-



**Figure 1.** Cyclic voltammograms for the TMPD/THF/ $\text{NaClO}_4$  system obtained with both platinum CSE (I) and UME (II).  $[\text{NaClO}_4]$ : a), b), d) and e)  $0.1 \text{ M}$ ; c)  $0.8 \text{ M}$ .  $[\text{TMPD}]$ : a), b), d) and e)  $9.3 \times 10^{-4} \text{ M}$ ; c)  $6.4 \times 10^{-3} \text{ M}$ . CSE area: a), b) and c)  $0.126 \text{ cm}^2$ . UME  $r$ : d)  $26.5 \mu\text{m}$ ; e)  $2.6 \mu\text{m}$ . v: a), b) and c)  $0.050 \text{ V s}^{-1}$ ; d) and e)  $0.005 \text{ V s}^{-1}$ .

tammogram obtained at 0.1 M NaClO<sub>4</sub> on a platinum CSE without compensation for the solution ohmic resistance ( $R_{\Omega}$ ) of the solution. As can be seen, it shows great distortion from the ohmic effect. When  $R_{\Omega}$  was compensated for with 1000  $\Omega$  the distortion diminished, but it was still very significant (see curve Ib). Considering that the value of the specific resistance ( $\rho$ ) decreases with the increase in the supporting electrolyte concentration<sup>20</sup>, it was possible to obtain almost non-distorted cyclic voltammograms only when the concentration of NaClO<sub>4</sub> was as high as 0.8 M and the  $R_{\Omega}$  of the solution was compensated for by 280  $\Omega$  using the positive feedback technique (curve Ic). Under these conditions, the values of  $k_f^0 = 0.018 \text{ cm s}^{-1}$  and  $(1 - \alpha) = 0.35$  were obtained<sup>10</sup>.

QSS voltammograms obtained with different platinum UMEs at 0.1 M NaClO<sub>4</sub> are shown in Fig. 1-II (curves d and e, respectively).

A useful diagnostic means for assessing reversibility is to check if the I - E curve satisfies the classical expression:  $E = E_f^0 \pm (RT/nF) \ln(i_L - i)/i$ <sup>8,17,21</sup>. Thus, a plot of  $\ln(i_L - i)/i$  vs. E for the curve II-d (the largest r is  $r = 26.5 \mu\text{m}$ ) shows a slope near to that theoretically expected for a reversible system.

The i-E curves obtained with the UME of smaller r are drawn out and shifted to more a positive potential than those obtained when microdisks of greater r are employed (curve IIe). In this case, a plot of  $\ln(i_L - i)/i$  vs. E shows a slope smaller than that theoretically expected for an ideal reversible system<sup>17</sup>. This is typical behavior for a process with kinetic or mixed control. Care should be taken to prevent the ohmic effect from having an influence on the process<sup>17,22</sup> as is the case under consideration (this will be discussed below). Thus, once the kinetic effects are detected by the shifts in voltammograms, the experimental data can be treated through Eqs. 1 and/or 2 to extract the kinetic parameters.

**Table 1.** Kinetic parameters calculated for the TMPD/THF/0.1 M NaClO<sub>4</sub> system. [TMPD]:  $9.3 \times 10^{-4} \text{ M}$ .  $D_{\text{TMPD}} = 1.53 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . T: 293 K.

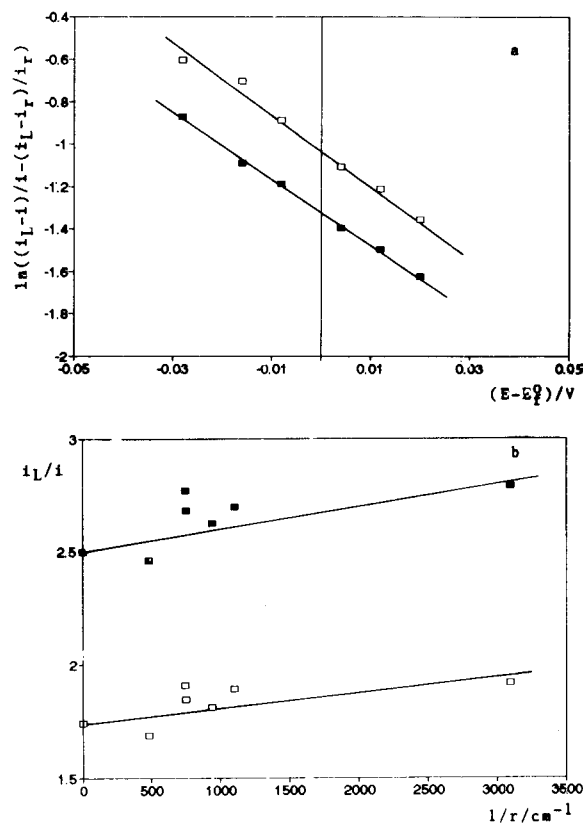
Equation number	$r/\mu\text{m}$	$k_f^0/\text{cm s}^{-1}$	$(1 - \alpha)^a$
1	20.6	0.124	0.33
1	12.8	0.041	0.51
1	12.5	0.058	0.44
1	11.0	0.053	0.43
1	9.5	0.056	0.44
1	2.6	0.165	0.57
2	—	0.180	0.69

<sup>a</sup> Average values of  $\overline{k_f^0} = (0.083 \pm 1.052) \text{ cm s}^{-1}$  and  $\overline{(1 - \alpha)} = (0.45 \pm 0.08)$  were calculated from values of  $k_f^0$  and  $(1 - \alpha)$  obtained through Eq. 1. Errors shown correspond to 95% confidence level.

The  $(i_L - i_r)/i_r$  term was calculated through the Nernst equation, using the  $E_{1/2}^r$  value determined from a QSS voltammogram obtained with the microdisk of the largest r ( $r = 26.5 \mu\text{m}$ ), the behavior of which corresponds to that expected for a reversible system, and the corresponding experimental  $i_L$  values for each UME. Plots of  $\ln[(i_L - i)/i - (i_L - i_r)/i_r]$  vs.  $(E - E_f^0)$  (Eq. 1) are shown in Fig. 2a. The kinetic parameters calculated through Eq. 1 are presented in Table 1.

Despite the fact that  $k_f^0$  and  $(1 - \alpha)$  values show some dispersion, with a large standard deviation in  $k_f^0$ , all values have statistical significance at a 90% confidence level according to a Q test of the experimental data. The average values,  $\overline{k_f^0}$  and  $\overline{(1 - \alpha)}$ , are given with a 95% confidence level according to the Student's test<sup>23</sup>. Rather large estimated errors ( $\pm 50\%$ ) have also been recently reported for the determination of charge-transfer rate constants of metalloporphyrins in a resistive medium ( $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{ClO}_4$  at 298 K)<sup>24</sup>.

The  $i_L/i$  vs.  $1/r$  plots at a given E (Eq 2) also show some degree of dispersion in the experimental  $i_L/i$  values. This can particularly be seen in Fig. 2b for medium range  $1/r$  values, where a set of UME of similar radii could be made.



**Figure 2.** a) Dependence of  $\ln[(i_L - i)/i - (i_L - i_r)/i_r]$  vs.  $(E - E_f^0)$ . r: (□) 12.5  $\mu\text{m}$ ; (■) 2.6  $\mu\text{m}$ ; b) Dependence of  $i_L/i$  vs.  $1/r$ . E: (■) 0.260 V; (□) 0.280 V. Solvent: THF. Supporting electrolyte: 0.1 M NaClO<sub>4</sub>. [TMPD]:  $9.3 \times 10^{-4} \text{ M}$ .

A regression analysis was performed on the data set, disregarding the two points that fall far from the trend (i.e.  $1/r \cong 750 \text{ cm}^{-1}$ ), for comparison with the previous method. From the correlation parameters obtained, a value of  $k_f^0$  a little higher than that determined through Eq 1 is obtained (see Table 1). The estimated error in  $k_f^0$  thus obtained should be at least similar to that obtained by the first method.

In addition, to check if an ohmic effect had any influence on the voltammetric curves, experiments on higher supporting electrolyte concentration solutions to increase the conductivity of the medium were performed. The kinetic parameters were also determined at 0.3 M NaClO<sub>4</sub>. The variation of  $k_f^0$  with the UME  $r$  (using Eq. 1) was similar to that observed with 0.1 M NaClO<sub>4</sub>. These results make evident that ohmic effects, if any, introduce no variations in the kinetic data derived from voltammetric responses.

It should be noted that the results obtained from the use of Eq. 2 for the extraction of kinetic parameters are somewhat more uncertain than those of Eq. 1 because the straight line is poorly defined. Although UME of different radii were used, several of them were of very similar  $r$ . Perhaps, a better correlation could be obtained using UME with  $r$  values widely spread along the range of  $r$ . This probably explains the higher values of  $k_f^0$  and  $(1 - \alpha)$  calculated through Eq. 2 with respect to those calculated through Eq. 1. In spite of both large deviations in  $k_f^0$  values determined through Eq. 1, and the dispersion of points in  $i_p/i$  vs.  $1/r$  plots (Fig. 2b), it is necessary to indicate that QSS voltammograms show good reproducibility when obtained starting from identical conditions.

For further comparison, we also calculated the kinetic parameters through the Mirkin *et al.* method<sup>6</sup>. This method is based on the determination of two easily accessible experimental parameters,  $(\Delta E_{1/4} = E_{1/4} - E_{1/2})$  and  $(\Delta E_{3/4} = E_{1/2} - E_{3/4})$ , where  $E_{1/2}$  is the experimental half-wave potential and  $E_{1/4}$  and  $E_{3/4}$  are voltammetric quartile potentials. All experimental  $\Delta E_{1/4}$  and  $\Delta E_{3/4}$  values obtained for UME of the large radii corresponded to empty cells in Table 2 of Ref. 6. These values of the quartile potentials can be associated with an almost reversible QSS voltammogram. However, values of  $\Delta E_{1/4} = 30.5 \text{ mV}$  and  $\Delta E_{3/4} = 31.5 \text{ mV}$  were calculated from the QSS voltammogram obtained with the smallest UME ( $r = 2.6 \mu\text{m}$ ). From the data of Table 2, Ref. 6, the values of the kinetic parameters can then be found at the intersection of the column and row. Thus, values of  $\lambda = 3.49$  (being  $\lambda = k_f^0 r/D_R$ ) and  $\alpha = 0.77$  were found. From these parameters, values of  $k_f^0 = 0.20 \text{ cm s}^{-1}$  and  $(1 - \alpha) = 0.23$  were obtained. They can thus be compared with those values calculated through the Galus method<sup>3</sup> if the smallest UME is considered, as can be seen in Table 1.

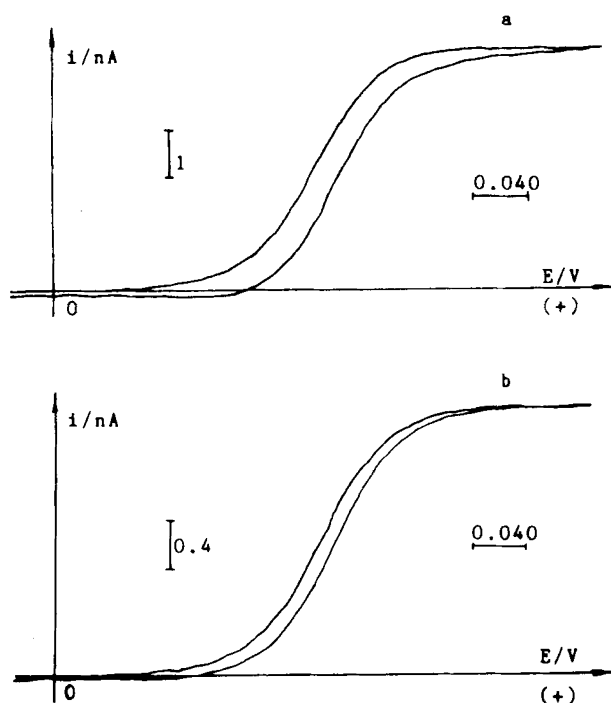
**Table 2.** Kinetic parameters obtained for the TMPD/n-BuOH/0.1 M TBAP system. [TMPD]:  $7.2 \times 10^{-4} \text{ M}$ .  $D_{\text{TMPD}} = 6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . T: 293 K.

Equation number	$r/\mu\text{m}$	$k_f^0/\text{cm s}^{-1}$ <sup>a</sup>	$(1 - \alpha)$
1	12.0	0.030	0.78
1	11.4	0.032	0.85
1	9.3	0.074	1.24
1	8.3	0.034	1
1	1.9	0.087	0.99
2	—	0.079	0.73

<sup>a</sup> Average value of  $k_f^0 = (0.051 \pm 0.033)$  was calculated from values of  $k_f^0$  obtained through Eq. 1. Errors shown correspond to 95% confidence level.

However,  $k_f^0$  values calculated using UME are larger than those determined with CSE for the same redox couple using conventional (transient) techniques, i.e. chronocoulometry and/or cyclic voltammetry. This behavior has already been observed by other authors for different redox couples<sup>17,24-26</sup>. This can be explained considering that a smaller cell constant and a diminished ohmic effect associated with UME lead to electrochemical responses not distorted by any ohmic drop, allowing the calculation of rate constants more reliable than those obtained with CSE, especially in highly resistive solvents<sup>24</sup>. An explanation for the difference in  $k_f^0$  has been attributed to a not fully compensated ohmic drop when working with CSE<sup>25</sup>, but a definitive conclusion has not been reached yet<sup>26</sup>.

The determination of the kinetic parameters for the TMPD/n-BuOH system deserves special consideration. The solubility of the most common supporting electrolytes in n-BuOH is smaller than in THF. Therefore, a high supporting electrolyte concentration could not be used in this medium. As such, the determination of  $k_f^0$ ,  $(1 - \alpha)$  and  $E_f^0$  under these conditions was not possible when using CSE<sup>14</sup> because cyclic voltammograms were greatly affected by an ohmic effect; their analysis was not possible even when the solution  $R_{\Omega}$  was electronically compensated. However, the QSS voltammograms for the TMPD/n-BuOH/0.1 M TBAP system on platinum UME could be easily obtained. This demonstrates that the use of UME notably reduces the potential ohmic drop. These voltammograms are shown in Figs. 3a and 3b. As it can be seen in these figures, QSS voltammograms for this system show a hysteresis greater than that observed in THF (Compare with Fig. 1-II d and e). The hysteresis phenomenon depends on the UME  $r$  being greater as  $r$  increases. A likely explanation for this behavior is given below. The analysis of these voltammograms through Eqs. 1 and 2 made it possible to obtain the tentative kinetic parameters, which are gathered in Table 2. The  $k_f^0$  values are lower than those determined for the THF/NaClO<sub>4</sub> system, but show a dispersion similar to that previously discussed for the THF/NaClO<sub>4</sub> system. However,  $(1 - \alpha)$  values determined in this medium are very



**Figure 3.** Cyclic voltammograms for the TMPD/n-BuOH/0.1 M TBAP. [TMPD]:  $7.24 \times 10^{-4}$  M.  $v = 0.005 \text{ V s}^{-1}$ . r: a) 26.5  $\mu\text{m}$ ; b) 1.9  $\mu\text{m}$ .

high considering that TMPD/TMPD<sup>•+</sup> is a simple redox couple.

These results and the pronounced hysteresis phenomenon in QSS voltammograms probably represent a more complicated system. This behavior can be tentatively explained considering a chemical follow-up reaction coupled to the electron transfer<sup>27</sup>. The precipitation of TMPD<sup>•+</sup>ClO<sub>4</sub><sup>-</sup>, the product of the oxidative electrolysis, at the electrode surface could be responsible for the abnormally high (near to one) values of the apparent anodic transfer coefficient (which makes no sense for a simple redox couple) and the hysteresis observed in this resistive medium. Another possible explanation for the high  $(1 - \alpha)$  determined values could be obtained by considering the reorganization energies via the Marcus theory<sup>10,13,28</sup>. In any case, a definitive conclusion is still not possible.

Cyclic voltammograms of solutions of TMPD/n-BuOH/0.1M TBAP at lower temperatures (i.e. 273 K) evidence that on the reverse (reductive) scan a peak-shaped rather than a sigmoidal-shaped curve is observed. However, this behavior is not evident when the temperature is increased (see Figs. 3a and 3b), though the hysteresis of the voltammograms is still large. Furthermore,  $\ln [(i_L - i)/i]$  vs.  $E$  plots for the forward scan at larger UME show slopes near to that theoretically expected for a reversible system, showing that the influence of the salt precipitation might not significantly affect this portion of voltammograms. This was basically the reason why we performed the kinetic

analysis through Eqs. 1 and/or 2, although the high  $(1 - \alpha)$  values calculated indicate that care should be taken in making a definitive conclusions. In addition, tentative  $k_f^0$  values for this system are in agreement with those expected, considering the solvent effect on the heterogeneous kinetics of this redox couple<sup>10</sup>.

## Conclusions

The use of QSSV to obtain the kinetic parameters of simple redox couples helps to overcome the difficulties arising from charging current and ohmic polarization, allowing kinetic determinations be done at supporting electrolyte concentrations lower than those used with CSE. Furthermore, it is important to note the possibility of obtaining tentative heterogeneous kinetic parameters in highly resistive media, as is discussed in this work for the n-BuOH/TBAP system, in spite of the fact that  $k_f^0$  values for this system may be affected by the difficulties discussed above. This was not possible through the use of CSE as the working electrodes.

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