

# Heterogeneous Electron Transfer Rate Constants of Viologen at a Platinum Disk Electrode

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The transfer of electrons to the dications of viologens including methyl viologen, diquat, benzyl viologen and n-butyl viologen was studied at the surface of a platinum disk electrode. The rate constants for the processes were determined and the effects of solvent, temperature and working electrode studied. The studies showed that the rate constants increase with temperature and the effect of solvent on the heterogeneous electron transfer rate constant is related to the polarity, dielectric constant and viscosity of the solvent and on the electrode material. Theoretical rate constants were calculated by considering the effects of barrier crossing probability and nuclear-frequency factor. Optimization of the theoretical values of rate constants at different reaction sites was carried out by comparing with experimental results. Activation parameters for the process were also obtained.

**Key Words:** and abbreviations used

$k^o$	Heterogeneous electron transfer rate constant
$k_{exp}^o$	Experimental rate constant for heterogeneous electron transfer process.
$MV^{++}$	Methyl viologen dication
$V^{++}$	Viologen dication
$NBV^{++}$	n-Butyl viologen dication
$BV^{++}$	Benzyl viologen dication
$BQ^{++}$	Diquat dication
$k_{Th}^o$	Theoretical rate constant for heterogeneous electron transfer process

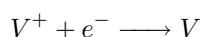
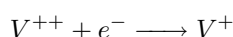
## Introduction

Quaternized pyridinium is an important part of several well-known reversible redox active species. Among the best examples are the  $NAD^+/NADH$  couple that act as an electron transfer catalyst in the respiratory chain<sup>1</sup> and the various viologens (N,N'-diaquaternized-4,4'-bipyridinium salts)<sup>2</sup>, which have been employed widely as redox mediators<sup>3,4</sup>, electrochromic materials,<sup>5-10</sup> electron transfer quenchers<sup>11-15</sup>, and as redox probes in self-assembled monolayers<sup>16-21</sup>, dendrimers<sup>22</sup>, silicates<sup>23-24</sup>, zeolites<sup>25,26</sup> and semiconductors<sup>27</sup>,

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As viologens have low redox potential with a significant degree of reversibility, they offer a suitable redox substrate for heterogeneous electron transfer studies and due to their importance, bipyridinium halides were selected for the present study to carry out work regarding their electrochemical behavior under different conditions. In this work heterogeneous electron transfer rate constants for the bipyridinium halide cations, i.e. methyl viologen (MV<sup>++</sup>), diquat (DQ<sup>++</sup>), benzyl viologen (BV<sup>++</sup>) and n-butyl viologen (NBV<sup>++</sup>) dications, were studied (See Figure 1 for structures). The reduction of a bipyridinium halide is a 2 step reduction process, the reduction of pyridinium dication to monocation and the subsequent reduction of monocation to neutral species.



The second electron transfer step has been discussed considering the heterogeneous electron transfer constants, both experimental and theoretical<sup>28</sup>. The effects of solvent and temperature on the  $k^o$  values have been observed. The reductions were carried out on a Pt disk electrode. The same studies are carried out for the first step using a Pt disk and hanging mercury drop electrode (HMD). In this case, besides temperature and solvent, the effect of electrode material on  $k_o$  is also observed.

The methods described by Nicholson<sup>29,30</sup>, (eq. 1) Kochi<sup>31</sup>, (eq. 2) and Gileadi<sup>32</sup>, (eq. 3) were used for the determination of  $k_{exp}^o$ . Nicholson<sup>29,30</sup> devised a method for the determination of heterogeneous electron transfer rate constant by relating peak separation with  $k_{s,h}$  and a function  $\psi$

$$\psi = \gamma k_{s,h} / (\pi a D_o)^{1/2}$$

where  $\gamma = D_o/D_R$ ,  $a = nFv/RT$ , and  $v$  is the scan rate.  $D_o$  and  $D_r$  are the diffusion coefficients for oxidized and reduced species. If  $\gamma = 1$

$$\psi = \frac{k^o}{(\pi D_o \frac{nFv}{RT})^{1/2}}$$

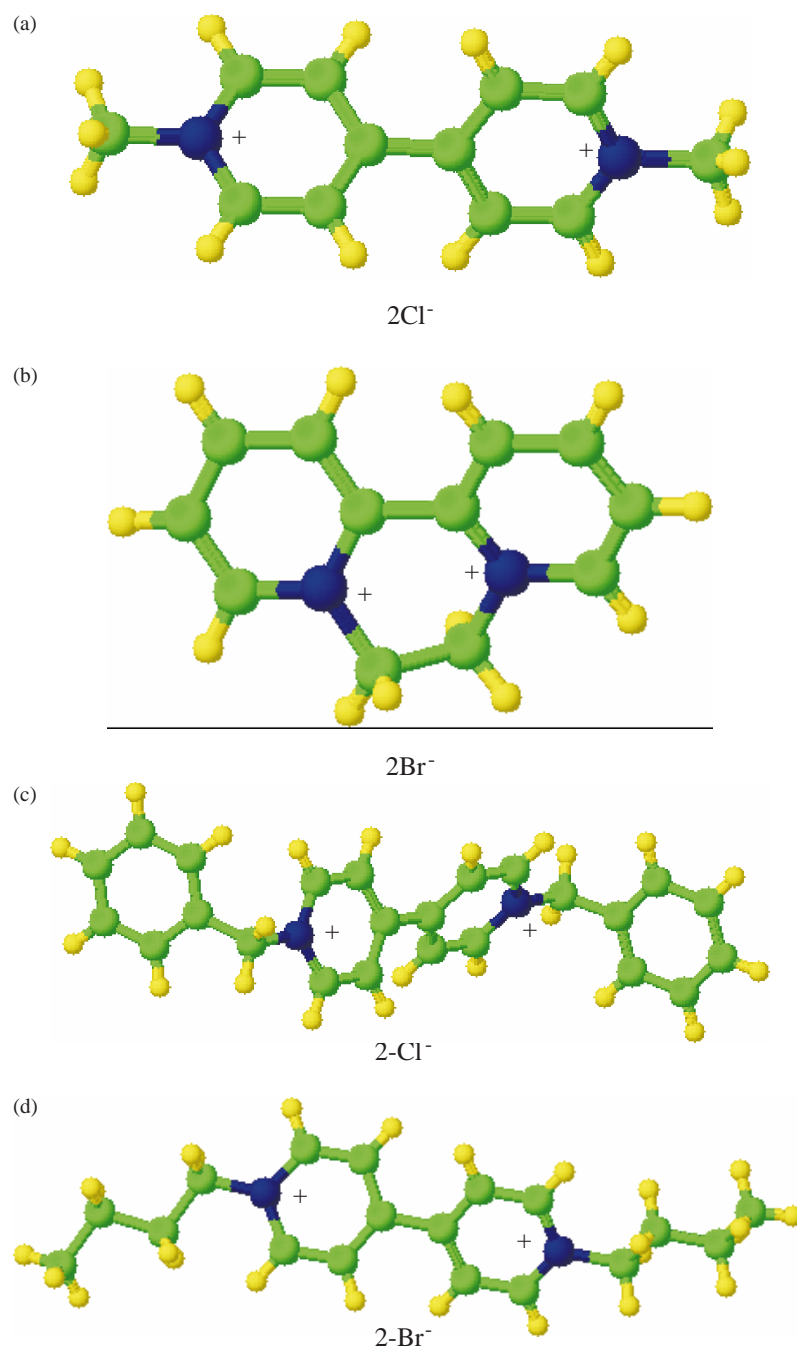
$$k^o = \psi \left[ \pi D_o \frac{nFv}{RT} \right]^{1/2} \quad (1)$$

The value of  $\psi$  is obtained from the working curve between  $\psi$  and peak separation,  $\Delta E_p$ . This method can be applied in the range of peak separation between 57 mv and 250 mv (in this range the electrode process is progressing from reversible to irreversible).

Like Nicholson, Kochi's method<sup>31</sup> is also based on peak separation

$$k^o = 2.18 \left[ \alpha v n F D_o / RT \right]^{1/2} \exp \left[ - \frac{\alpha^2 n F \Delta E_p}{RT} \right] \quad (2)$$

where  $\alpha$  is a dimensionless parameter known as electron the transfer coefficient,  $n$  is the number of electrons transferred and  $DP_o$  is the diffusion coefficient of the oxidized species in  $\text{cm}^2 \cdot \text{s}^{-1}$   $\Delta E_p = E_p^c - E_p^a$ . For the reversible reaction the value of  $\alpha$  is 0.5.



**Figure 1.** Structures of Viologens compounds (a) 1,1'-dimethyl-4,4'-bipyridinium dichloride or Methyl viologen or paraquat (MV) (b) 1,1'-dimethyl-2,2'-bipyridinium dibromide or Diquat (DQ) (c) 1,1'-dibenzyl-4,4'-bipyridinium dichloride or benzyl viologen (BV) (d) 1,1'-n-butyl-4,4'-bipyridinium dibromide or n-butyl viologen (NBV).

Gileadi<sup>32</sup> suggested another simple method for the determination of the heterogeneous electron transfer rate constant that does not require the value of peak separation. When a reversible heterogeneous electron transfer process is studied at different scan rates, the process will change from reversible to irreversible as the scan changes from slow to fast. In this case if  $E_p^c$  is plotted against the logarithm of scan rate, a linear curve at a low scan rate and an ascending curve at a high scan rate are obtained. If both are extrapolated they intersect at a point corresponding to the critical scan rate,  $v_c$ , which has a linear relation with  $k^o$

$$\log k^o = -0.48\alpha + 0.52 + \log \left[ nF\alpha v_c D_o / 2.303RT \right]^{1/2}. \quad (3)$$

This method may also be used for systems where an anodic peak is absent.

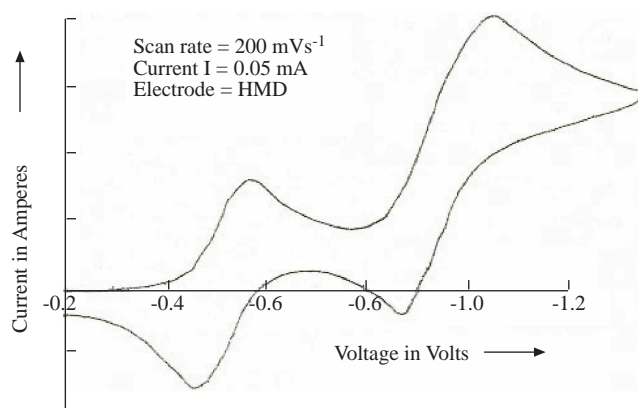
Theoretical values of rate constants for the halides have been calculated in given solvent mixtures by applying a modified version of the Marcus equation.<sup>33-35</sup>

$$k^o = \kappa \delta \nu_n Z_{het} \exp \left[ -\frac{\Delta G^*}{k_B T} \right] \quad (4)$$

where  $\kappa$  is the barrier crossing probability,  $\delta$  is the distance of the electrode from the reaction site,  $\nu_n$  is the solvent dependent nuclear frequency factor,  $\Delta G^*$  is the free energy of activation,  $Z_{het}$  is the collision frequency of reactant molecules,  $k_B$  is the Boltzman constant and T is the temperature of the reaction.  $\kappa$  depends upon the work function of metal from which the electrode is made and its values for a platinum disk electrode and hanging mercury drop electrode are 5.65 and 4.98 e.V<sup>36</sup>, respectively.

## Experimental

Experimental rate constants for heterogeneous transfer of electron ( $k_{exp}^o$ ) to the dications of methyl viologens (MV<sup>++</sup>), benzyl viologen (BV<sup>++</sup>), diquat viologens (DV<sup>++</sup>) and n-butyl viologens (NBV<sup>++</sup>) were determined by using Nicholson, Kochi and Gileadi's methods based upon the cyclic voltammetric (CV) technique. A Beckman platinum disk (Pt disk) electrode of diameter 1 mm and hanging mercury drop (HMD) electrode were used as working electrodes. The HMD electrode was formed by sealing a gold wire of diameter 1.5 mm in a glass capillary, covered with mercury, using copper wire for external connection. 30:70% v/v mixtures of water with formamide (FM), with dimethyl formamide (DMF) and with dimethyl sulfoxide (DMSO) were used as solvents. The same experimental conditions and instrumentations were used as reported for the reduction of monocations of viologens (V<sup>++</sup> and V<sup>+</sup>) at a Pt disk electrode<sup>28</sup>. The cyclic voltammogram recorded for MV<sup>++</sup> in the DMF and water mixture is shown in Figure 2.



**Figure 2.** Cyclic Voltammogram for reduction process of  $MV^{++}$  in DMF and water mixture.

## Results and Discussion

The effect of temperature, solvent parameters and electrode material on  $k^o$  have been discussed below. The experimental rate constants  $k_{exp}^o$  are listed in Tables 1-3. Table 1 gives the  $k_{exp}^o$  for the reduction of  $MV^{++}$  at 5 different temperatures at the Pt electrode. Table 2 lists the  $k_{exp}^o$  at 298 K for 3 different viologens in 3 solvents using 3 methods at 298 K and Table 3 contains the  $k_{exp}^o$  at the Pt disk and HMD electrodes for the 4 viologens in 3 different solvents at 298 K.

**Table 1.** Values of  $k_{exp}^o$  for the reduction process of  $MV^{++}$  to  $MV^+$  at the Pt disk electrode.

Solvent mixture	$k_{exp}^o \times 10^3 / \text{cm s}^{-1}$ at temperature				
	293 K	298 K	303 K	308 K	313 K
DMSO	$0.53 \pm 0.013$	$0.74 \pm 0.020$	$00.98 \pm 0.05$	$01.46 \pm 0.02$	$01.89 \pm 0.08^G$
	$2.10 \pm 0.270$	$3.10 \pm 0.200$	$04.90 \pm 0.40$	$08.30 \pm 0.35$	$11.90 \pm 0.01^N$
	$1.44 \pm 0.150$	$2.10 \pm 0.280$	$02.90 \pm 0.40$	$03.96 \pm 0.75$	$05.50 \pm 1.00^K$
DMF	$0.65 \pm 0.004$	$0.97 \pm 0.004$	$01.27 \pm 0.01$	$01.74 \pm 0.01$	$02.23 \pm 0.04^G$
	$2.00 \pm 0.100$	$4.00 \pm 0.050$	$06.30 \pm 0.05$	$11.80 \pm 0.32$	$51.00 \pm 7.22^N$
	$2.10 \pm 0.170$	$2.90 \pm 0.150$	$04.10 \pm 0.30$	$05.60 \pm 0.40$	$09.00 \pm 0.30^K$
FM	$0.71 \pm 0.010$	$1.00 \pm 0.012$	$01.38 \pm 0.02$	$01.87 \pm 0.03$	$02.40 \pm 0.05^G$
	$5.70 \pm 0.230$	$9.60 \pm 0.160$	$18.30 \pm 0.60$	$29.00 \pm 0.26$	$55.50 \pm 2.30^N$
	$3.60 \pm 0.240$	$4.80 \pm 0.470$	$06.10 \pm 0.33$	$08.00 \pm 0.45$	$10.40 \pm 0.87^K$

$k_{exp}^o$  is calculated using the (G) Gileadi, (N) Nicholson and (K) Kochi methods.

### Temperature effect

It has been observed from Table 1 that  $k_{exp}^o$  for electron transfer to the dication of methyl viologen ( $MV^{++}$ ) at the surface of Pt disk increases with the increase of temperature. This trend is in agreement with the results reported for the reduction of monocation of these viologens at the surface of Pt disk<sup>28</sup> and with the results reported for other systems<sup>38</sup>. From the data mentioned in Table 4 it is observed that theoretical calculations also show the same trend for the values of rate constants ( $k^o$ ).

An increase in temperature decreases the height of the potential energy barrier<sup>39</sup>, thus facilitating the electron transfer process at the surface of the electrode. Moreover, an increase in temperature increases the kinetic energy of  $V^{++}$ , which may be accompanied by an increase in the rate of diffusion and eventually resulting in an increase in  $k_{\text{exp}}^o$  value. A dimerization reaction should also be considered in the chemistry of viologens ions and temperature may affect the dimerization of  $V^{++}$  inversely. With the increase in kinetic energy dimerization decreases and more  $V^{++}$  may become available for enhancing electron transfer at the surface of the electrode.

## Solvent effect

In solvent mixtures the experimental  $k^o$ , for electron transfer to  $V^{++}$  at the surface of the Pt disk, exhibited the following trend:  $k_{FM}^o > k_{DMF}^o > k_{DMSO}^o$  (see Table 2). As a higher value of polarity and dielectric constant favor the electron transfer reactions<sup>40,41</sup>, the FM mixture, being the most polar mixture with highest dielectric constant<sup>28</sup> among the solvents used, exhibits the highest values of  $k_{\text{exp}}^o$ . DMSO and DMF mixtures have similar polarities and dielectric constants but different values of viscosities, which affects the rate constants<sup>42</sup>. The lower viscosity of the DMF mixture justifies high values of  $k_{\text{exp}}^o$  in DMF. A similar trend was also observed in the reduction of pyridinium monocation<sup>28</sup>.

**Table 2.** Values of  $k_{\text{exp}}^o$  for the reduction process of  $V^{++}$  to  $V^+$  at 298K at the Pt disk electrode.

Solvent Mixture	Dication of Viologen	$k_{\text{exp}}^o \times 10^3 / \text{cm s}^{-1}$ evaluated using		
		Gileadi Method	Nich. Method	Kochi Method
DMSO	DQ <sup>++</sup>	0.50 ± 0.007	1.58 ± 0.004	1.30 ± 0.150
DMF		0.60 ± 0.007	4.30 ± 0.047	3.00 ± 0.900
FM		1.43 ± 0.030	6.50 ± 0.080	4.20 ± 1.500
DMSO	BV <sup>++</sup>	0.90 ± 0.02	3.00 ± 0.03	2.00 ± 0.60
DMF		1.70 ± 0.05	5.00 ± 0.05	2.00 ± 0.40
FM		2.30 ± 0.04	7.00 ± 0.01	3.00 ± 0.70
DMSO	NBV <sup>++</sup>	0.23 ± 0.050	0.70 ± 0.008	0.50 ± 0.090
DMF		0.30 ± 0.010	3.00 ± 0.040	1.70 ± 0.200
FM		0.80 ± 0.070	4.50 ± 0.020	2.30 ± 0.800

MV<sup>++</sup> (dication of methyl viologen), DQ<sup>++</sup> (dication of diquat), BV<sup>++</sup> (dication of benzyl viologen), NBV<sup>++</sup> (dication of n-butyl viologen).

## Effect of electrode material

The rate constant for the electron transfer process also depends upon the nature of the material of the electrode, as the change of the electrode material changes the energy barrier which in turn affects the  $k^o$  value. It is observed (see Table 3) that  $k^o$  for electron transfer from the Pt disk is smaller than the  $k^o$  for the process at HMD electrode. The work function for HMD electrode is 4.49 e.V<sup>43</sup>, which is obviously less than the work function of the Pt disk (5.65 e.V.). The potential energy barrier height has a larger value for the Pt disk compared to HMD, and  $k^o$  is inversely proportional to the barrier maximum. Therefore it may be expected that  $k^o$  values for electron transfer from the Pt disk should be smaller than the  $k^o$  for the

process at HMD, and the experimental results are in agreement with the expected trend. The  $k_{\text{exp}}^o$  values show a trend similar to that reported for another system using the same electrode<sup>44</sup>.

**Table 3.** Comparison between  $k_{\text{exp}}^o$  for viologens at HMD and at the Pt disk electrode at 298 K.

Dication of Viologen	$k_{\text{exp}}^o \times 10^3 / \text{cm s}^{-1}$ in					
	DMSO Mixture at		DMF Mixture		FM Mixture	
	Pt Disk	HMD	Pt Disk	HMD	Pt Disk	HMD
MV <sup>++</sup>	0.74	04.47	0.97	05.95	1.00	07.39 <sup>G</sup>
	3.10	05.40	4.00	11.60	9.60	32.10 <sup>N</sup>
	2.10	04.00	2.90	09.19	4.80	18.30 <sup>K</sup>
DQ <sup>++</sup>	0.50	06.2	0.60	06.6	1.43	10.0 <sup>G</sup>
	1.58	17.2	4.30	16.5	6.50	29.0 <sup>N</sup>
	1.30	04.0	3.00	09.2	4.20	18.3 <sup>K</sup>
BV <sup>++</sup>	0.9	12.0	1.7	17.6	2.3	45.0 <sup>G</sup>
	3.0	10.6	5.0	23.7	7.0	21.6 <sup>N</sup>
	2.0	07.5	2.0	08.6	3.0	22.4 <sup>K</sup>
NBV <sup>++</sup>	0.23	02.1	0.30	12.2	0.80	19.2 <sup>G</sup>
	0.70	06.0	3.00	13.4	4.50	28.6 <sup>N</sup>
	0.50	03.0	1.70	06.7	2.30	15.5 <sup>K</sup>

MV<sup>++</sup> (dication of methyl viologen), DQ<sup>++</sup> (dication of minquat), BV<sup>++</sup> (dication of benzyl viologen)  $k_{\text{theor}}^o$  calculated from eq. (4) at (a)  $R_e = 2(r+L)$ , (b)  $R_e = 2r$ , where  $r$  represent the radii of molecules.  $L$  is the length of the solvent molecule.

**Table 4.** Values of  $k_{\text{theor}}^o$  for the reduction process of MV<sup>++</sup> to MV<sup>+</sup> at the Pt disk electrode.

Distance of Reaction site $\delta / \text{nm}$	$k_{\text{theor}}^o \times 10^3 / (\text{cm.s}^{-1})$ in Solvent Mixture					
	DMSO Mixture at $R_e =$		DMF Mixture at $R_e =$		FM Mixture at $R_e =$	
	$2(r+L)$	$2r$	$2(r+L)$	$2r$	$2(r+L)$	$2r$
0.50	0.90	3.72	1.41	6.10	0.79	3.27 <sup>a</sup>
	1.55	6.14	2.41	9.96	1.42	5.64 <sup>b</sup>
	2.64	10.06	3.85	15.3	2.41	9.23 <sup>c</sup>
0.55	0.34	1.40	0.52	2.25	0.30	1.23 <sup>a</sup>
	0.58	2.30	0.89	3.67	0.53	2.12 <sup>b</sup>
	0.98	3.76	1.42	5.63	0.90	3.46 <sup>c</sup>
0.60	0.13	0.54	0.20	0.86	0.11	0.48 <sup>a</sup>
	0.22	0.88	0.34	1.40	0.21	0.82 <sup>b</sup>
	0.38	1.45	0.54	2.14	0.35	1.34 <sup>c</sup>
0.65	0.05	0.21	0.08	0.33	0.04	0.19 <sup>a</sup>
	0.09	0.35	0.13	0.54	0.08	0.32 <sup>b</sup>
	0.15	0.57	0.21	0.83	0.14	0.52 <sup>c</sup>

$k_{\text{theor}}^o$  calculated from eq.(4) at temperature (a) 293 K, (b) 303 K, (c) 313 K

## Theoretical results

Theoretical values of  $k^o$  for the first reduction of viologen dications are calculated by applying eq. (4) and are shown in Table 4. Variations in theoretical values for  $k^o$  are similar to  $k_{\text{exp}}^o$  (i.e. values of  $k_{\text{th}}^o$  for the Pt disk are smaller than  $k_{\text{th}}^o$  values for HMD).

A comparison between  $k_{\text{th}}^o$  and  $k_{\text{exp}}^o$  is shown in Table 5. It is observed that the experimental results are in good agreement with the theoretical results at some specific assumed distances of reaction sites from the electrode surface. In this way, an approximation concerning the location of reaction site can also be made. In these calculations the reaction site varied from 0.5 to 0.65 nm. Elsewhere a value of 6 nm was obtained by solving the Langevin function<sup>45</sup>.

**Table 5.** Comparison of values of experimental and theoretical rate constants at 298 K.

Monocation of viologen	Results from	$k^o \times 10^3 / \text{cm s}^{-1}$ in		
		DMSO mixture	DMF mixture	FM mixture
MV <sup>++</sup>	Experiment	$0.74 \pm 0.020$	$0.97 \pm 0.004$	$1.00 \pm 0.012$
	Theory	$0.69^{b,f}$	$1.10^{b,f}$	$1.06^{a,d}$
DQ <sup>++</sup>	Experiment	$0.50 \pm 0.007$	$0.60 \pm 0.007$	$1.43 \pm 0.030$
	Theory	$0.53^{b,f}$	$0.42^{a,e}$	$1.25^{b,e}$
BV <sup>++</sup>	Experiment	$0.90 \pm 0.020$	$1.70 \pm 0.050$	$2.30 \pm 0.040$
	Theory	$0.82^{a,f}$	$1.82^{a,f}$	$2.46^{c,d}$
NBV <sup>++</sup>	Experiment	$0.23 \pm 0.050$	$0.30 \pm 0.010$	$0.80 \pm 0.070$
	Theory	$0.22^{a,g}$	$0.35^{a,g}$	$1.00^{c,d}$

$R_e = 2(r+L)$ , (b)  $R_e = 2r$ , (c)  $R_e = \infty$ , (d)  $\delta = 0.5$  nm, (e)  $\delta = 0.55$  nm, (f)  $\delta = 0.60$  nm, (g)  $\delta = 0.65$  nm.

## Activation parameters

Activation parameters for the electron transfer process from the Pt disk to V<sup>++</sup> are reported in Table 6. The activation parameters were obtained by plotting  $-\ln k_{\text{exp}}^o T^{-1/2}$  vs.  $T^{-1}$ . The values of  $\Delta G^*$  and  $\Delta S^*$  were obtained from the plots and  $\Delta H_{\text{exp}}$  were calculated from  $\Delta H = \Delta G + T\Delta S$ <sup>37</sup>. The rate constants used in the plotting were the  $k_o$  values calculated using Gileadi's method at the Pt disk electrode.

**Table 6.** Activation parameters for the first reduction of V<sup>++</sup> at the Pt disk electrode at 298 K.

Act. Param. x 10 / e.v	Solvent mixture	Dication			
		MV <sup>++</sup>	DQ <sup>++</sup>	BV <sup>++</sup>	NBV <sup>++</sup>
$\Delta G_{\text{exp}}^*$	DMSO	4.9	5	5	9.6
	DMF	4.68	4.8	6	6.4
	FM	4.67	4.9	4.7	7.3
$\Delta H_{\text{exp}}^*$	DMSO	4.99	5	5.1	9.6
	DMF	4.67	4.8	6	6.5
	FM	4.66	4.9	4.7	7.3
$\Delta S_{\text{exp}}^*$	DMSO	0.003	0.0032	0.004	0.02
	DMF	0.002	0.0024	0.007	0.008
	FM	0.002	0.0034	0.003	0.01



## Conclusion

In this work the heterogeneous electron transfer rate constants ( $k^o$ ) for the first reduction process of 4 viologens were determined on a Pt electrode and HMD electrode using the CV technique. It was observed that rate constants increase with the increase in temperature. The measurements were carried out in 3 solvent mixtures and it was observed that solvent of higher dielectric constants and polarity (formamide in this case) favors electron transfer, leading to a higher value of  $k^o$ . In the case of solvents with similar dielectric constants and polarity values the effect of viscosity should also be taken into account as solvents of lower viscosities favor electron transfer. The heterogeneous electron transfer rate constants determined on the Pt disk electrode were smaller than those determined for the HMD electrode. This is explained on the basis of the work function of the metal, i.e. smaller values of work function favor electron transfer easily. Theoretical values of heterogeneous electron transfer were also calculated using the Marcus theory. A reasonable agreement between the experimental and theoretical values was observed.

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