

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

Naheed Kaukab BHATTI, M. Sadiq SUBHANI, Ather Yaseen KHAN,
Rumana QURESHI*, Abdur RAHMAN
Chemistry Department, Quaid-i-Azam University, Islamabad-PAKISTAN
e-mail: rumana_q@yahoo.co.in

Received 09.07.2004

Experimental values of rate constants for the heterogeneous transfer of electrons to methyl viologen, diquat viologen, benzyl viologen and n-butyl viologen monocations were determined. The process was studied at the surface of a platinum disk in mixtures of water with different aprotic solvents at different temperatures. Theoretical rate constants were evaluated using Marcus' equation, which also contains barrier crossing probability and nuclear frequency. A comparison was made between the theoretical and experimental values of rate constants.

Key Words: Viologen monocations, experimental rate constant for heterogeneous electron transfer process, theoretical rate constant for heterogeneous electron transfer process.

Introduction

Bipyridinium halides belong to an important class of compounds with potential applications as herbicides^{1,2}, monomers in polymer film formation³, mediating and reducing agents, components of secondary batteries and in the investigation of solar or photochemical processes leading to the investigation of photochemical cells^{4-7,8}, and in investigations of photochromism produced by electron transfer⁹. Furthermore, viologens are used in the paper industry for producing colored paper¹⁰, in electrochromic printing applications¹¹, and for color modulation by additives for photochromic properties³. Viologens are also used to enhance the quantum efficiency of the electroluminescence of LED^{12,13}. Due to their low redox potential with a significant degree of reversibility they can be considered suitable redox substrates for heterogeneous electron transfer studies. Extensive work other than on heterogeneous electron transfer has been reported in the literature¹⁴.

The study of rates of electron transfer reactions at the electrode electrolyte solution interface is a fundamental issue in electrochemistry. Information on the kinetics of the reaction at the surface of the electrode is of great importance for a basic understanding of the kinetics of heterogeneous electron transfer reactions because electrode processes are considered to occur commonly via a reaction pathway involving specifically adsorbed intermediates¹⁵.

*Corresponding author

A reversible electron transfer reaction with a single elementary step may be represented as



where Ox and Red. are oxidized and reduced forms of electro-active species. For the experimental determination of rate constants for reversible or quasi-reversible reactions at the electrode surface various techniques can be used, including A.C. polarography, cyclic voltammetry and other similar techniques. Marcus^{16,17}, Hush^{18,19}, Levich²⁰ and Dogonadze²¹ have developed theories to explain the electron transfer reaction mechanism.

In the present work, Nicholson's^{22,23}, Kochi's²⁴ and Gileadi's²⁵ equations are used for the determination of experimental values of the rate constant for the electron transfer process.

Nicholson proposed a relation between a function ψ (which depends on peak separation) and the rate constant (k^o)

$$\psi = k^o \left(\frac{RT}{\pi n F D v} \right)^{1/2} \quad (2)$$

Kochi²⁴ has reported the following expression

$$k^o = 2.18 \left[\frac{\alpha v n F D}{RT} \right]^{1/2} \exp \left[-\frac{\alpha^2 n F \Delta E_p}{RT} \right] \quad (3)$$

A comparatively simpler method for the evaluation of k^o is Gileadi's²⁵ method.

$$\log k^o = -0.48\alpha + 0.52 + \log \left[\frac{n F \alpha v_c D_o}{2.303 RT} \right]^{1/2} \quad (4)$$

where α is a dimensionless parameter, known as the electron transfer coefficient, n is the number of electrons transferred, v_c is the critical scan rate, ΔE_p is the peak separation ($E_p^a - E_p^c$) and D is the diffusion coefficient in cm^2s^{-1} .

Marcus suggested the following expression for the theoretical calculation of k^o

$$k^o = k_{el} Z_{het} \exp \left[-\frac{\Delta G^*}{k_B T} \right] \quad (5)$$

where $k_{el} = 1$ for an adiabatic process, Z_{het} is the collision frequency of a reactant molecule on the surface of the electrode, ΔG^* is the free energy of activation for forward electron transfer, and k_B and T have the usual significance. A kinetic gas theory expression is used for Z_{het} . If a distance parameter is included in equation (5) then it becomes

$$k^o = k_{el} Z_{het} \delta \exp \left[-\frac{\Delta G^*}{k_B T} \right] \quad (6)$$

$$Z_{het} = \left(\frac{k_B T}{2\pi m} \right)^{1/2} = \left(\frac{RT}{2\pi m N_L} \right)^{1/2} = \left(\frac{RT}{2\pi M} \right)^{1/2} \quad (7)$$

where N_L is Avogadro's number, m and M are the reduced and molecular mass of the reacting species and δ is the distance between the electrode and reaction site.

The value of ΔG^* is given by Marcus^{16,17} as

$$\Delta G^* = w^O + [\lambda + w^R - w^O]^2 / 4\lambda \quad (8)$$

w^O and w^R are the work required to transport oxidized and reduced species from the bulk of the solution to the reaction site. λ is the reorganization energy, composed of the inner reorganization energy (λ_I) and the solvent reorganization energy (λ_o).

$$\lambda = \lambda_i + \lambda_o \quad (9)$$

The magnitude of λ_o can be obtained from the following equation

$$\lambda_o = \frac{e^2 N_L}{8\pi\epsilon_o} g(r.Re) \left[\frac{1}{n^2} - \frac{1}{\epsilon_s} \right] \quad (10)$$

where r is the radius of the reactant molecule and Re is the distance from the molecule's center the image charge on the electrode, e is the electronic charge, N_L is Avogadro's constant, ϵ_o is vacuum permittivity, n is the refractive index and ϵ_s is the static dielectric constant of the solvent.

Presently Marcus' equation (6) has been modified to equation (11) by introducing the barrier crossing activation parameter (κ), which accounts for the probability of an electron to cross the potential barrier

$$k^o = \kappa \delta Z_{het} \exp \left[-\frac{\Delta G^*}{k_B T} \right] \quad (11)$$

Equation (11) can be modified further to equation (12) to incorporate the nature of the solvent in the rate expression in terms of effective nuclear frequency (ν_n).

$$k^o = \kappa \delta \nu_n Z_{het} \exp \left[-\frac{\Delta G^*}{k_B T} \right] \quad (12)$$

where δ is the distance between the electrode and the reaction plane (OHP). If λ_i has less than 10% contribution to λ then it is negligible, thus $\lambda = \lambda_o$, and $\nu_n = \nu_o$.

$$\nu_n = \left(\frac{\nu_o^2 \lambda_o + \nu_i^2 \lambda_i}{\lambda_i + \lambda_o} \right)^{1/2} \quad (13)$$

and

$$\nu_o = \tau_L^{-1} \left(\lambda_o / 16\pi R T \right)^{1/2} \quad (14)$$

where

$$\tau_L^{-1} = \left(\epsilon_\infty / \epsilon_s \right) \tau_D \quad (15)$$

and

$$\tau_D = 3V_m\eta/RT \quad (16)$$

τ_D is Debye relaxation time, V_m is molar volume and ε_∞ is the dielectric constant of the solvent at high frequency. In terms of a 2 mode model, ν_n is related to ν_o and ν_i (molecular vibrations).

Due to their importance as mentioned above, bipyridinium halides were selected for the present studies to carry out work regarding their electrochemical behavior under different conditions. k^o of a series of 4 bipyridinium monocations reduction processes are measured here using different solvents at different temperatures by the methods described by Nicholson^{22,23} Kochi²⁴ and Gileadi²⁵.

Theoretical values of rate constants for these compounds are calculated under the experimental conditions by applying Marcus' equation (5) and a modified version of Marcus' equation (11). For better agreement between theoretical and experimental values of k^o equation (12) was used in combination with equations (13) and (14). The values of rate constants obtained using equation (12) in combination with equations (13) and (14) are in best agreement with the experimentally calculated values; therefore only results obtained by this method are presented in this paper.

Experimental

Chemicals Tetra butyl ammonium perchlorate (99% TBAP) from Fluka Chemicals was used as the supporting electrolyte without further purification. Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and formamide (FM) of AR grade from BDH Chemicals Ltd, Poole, England, were used. DMF was further purified by the method reported in the literature²⁶ and DMSO and FM were used without further purification. Triply distilled water was used throughout the studies. In the present study compounds donated by ICI, Runcorn, England, were used without further purification. Their names and structures and abbreviations of their cations (as used in the rest of the text) shown in Figure 1 (in the given structures blue, green and yellow balls represent nitrogen, carbon and hydrogen atoms, respectively).

Electrochemical measurements All these measurements were performed with 3 electrode system consisting of a Beckman platinum disk electrode of diameter 5 mm as the working electrode, a reference saturated calomel electrode (SCE) type 232 and a Beckman platinum wire electrode of diameter 1 mm as the counter electrode. A double walled electrochemical cell model (K65, PARC) along with cell top model (K66, PARC) having specific holes for the 3 electrode system, thermometer and N₂ inlet was used as the electrochemical cell. A polarographic analyzer Model 174A Princeton and x-y recorder model Princeton RE0074 were used for recording scan rates ranging from 50 to 500 mVs⁻¹. For high scan rates ranging from 1 to 500 Vs⁻¹ the potentiostat model 173 (EG & PAR) coupled with a plarographic analyzer (EG & G PAR) and a digital coulometer model 179 (EG & G PAR) were used. Voltammograms recorded for all viologen compounds show 2 peaks, the first peak corresponding to the reduction of dication to monocation and second to the reduction of monocation to neutral species as (Figure 2)

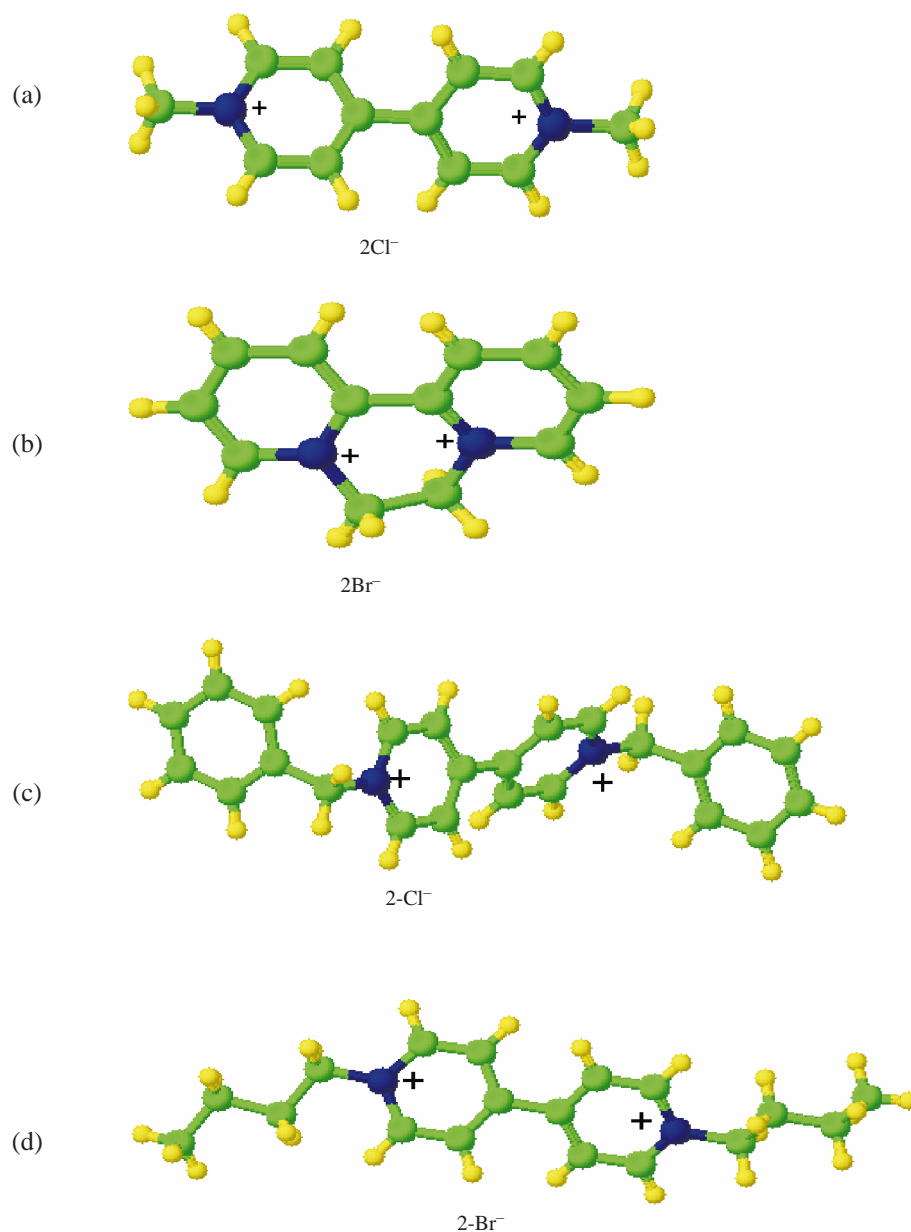
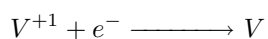
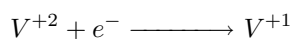


Figure 1. Structures of viologens compounds (a) 1,1'-dimethyl-4,4'-bipyridinium dichloride or methyl viologen or paraquat (MV) (b) 1,1'-dimethyl-2,2'-bipyridinium dibromide or diquat (DQ) (c) 1,1'-dibenzyl-4,4'-bipyridinium dichloride or benzyl viologen (BV) (d) 1,1'-n-butyl-4,4'-bipyridinium dibromide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



Higher scan rate observations were recorded with the help of a Tetrax storage oscilloscope model 5103N with differential amplifier model 5A20 and time base/amplifier model 5B10N. The electrochemical probe model 178 (EG & G PAR) and the high input impedance electrometer amplifier were used as a buffer

between the reference electrode and the potentiostat input.

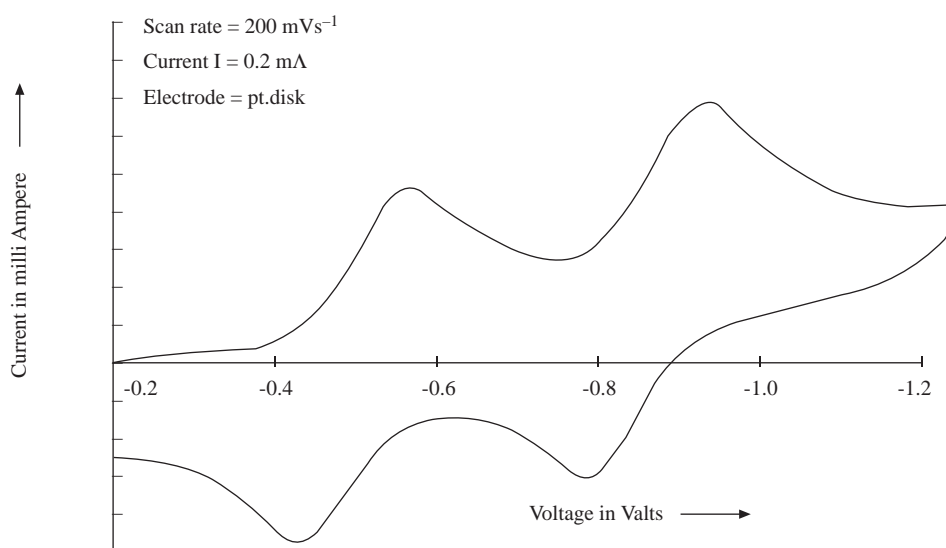


Figure 2. Cyclic voltammogram for reduction processes of MV⁺⁺ to MV in DMF water mixture.

Temperature Control For the thermostat model lauda K4R was attached to the electrochemical cell to maintain the temperature by internal circulation arrangements.

Purification of N₂ Gas All cyclic voltammetric measurements were carried out under nitrogen atmosphere to avoid interference caused by oxygen. Commercial nitrogen was purified by passing it through a series of traps (to remove dissolved oxygen and water vapors) containing chromium chloride solution, pyragallol solution, silica gel, concentrated sulfuric acid and the solvent under study.

Measurements of Peak Separation and Current Standard heterogeneous rate constants of viologens were determined at 5 temperatures (293, 298, 303, 308 and 313 K) in a solvent mixture containing water and given aprotic solvent (DMF, FM, and DMSO) in 30:70% v/v ratio. To evaluate k^o , cyclic voltammograms were recorded at scan rates ranging from 0.05 to 500Vs⁻¹, using 0.1 M solution of supporting electrolyte and 1 mM solution of reacting species. The rates were evaluated from the difference of the anodic and cathodic peak potentials, i.e. ($\Delta E_p = E_p^a - E_p^c$) measured from the cyclic voltammogram. Diffusion coefficient values, required to evaluate k^o by the methods described above, were calculated from the observed peak current using equation (17)²⁶

$$i_p = (2.69 \times 10^5) n^{3/2} A C_o D_o^{1/2} v^{1/2} \quad (17)$$

where i_p is peak current, A is the area of the electrode, F is Faraday, C_o is the concentration, v is the scan rate and D_o is the diffusion coefficient of the reacting species.

Results and Discussions

The electrochemical experiments were carried out in a 30:70% (V/V) mixture of water and respective solvents. The solvents used were DMSO, DMF, and FM. The characteristic properties of the solvents mixtures, i.e. refractive index (n_D), dielectric constant (ϵ_s), density (ρ) and viscosity (η), were calculated and are listed in Table 1. The values of k_{exp}^o for the reduction of monocations in 3 solvents at different

temperatures using the 3 different methods are given in Table 2 and 3. The variation of the rate constants with temperature, solvent and method is discussed below.

Table 1. Properties of solvents mixture at different temperatures.

Solvent mixture ^a	Temp. /K	Refractive Index n_D	Dielectric Constant ϵ_s	Density $\rho/ \text{g.cm}^{-3}$	Viscosity η/ cp
DMSO	293	1.3864	68.6	1.036	1.442
	298	1.3853	67.0	1.034	1.301
	303	1.3840	65.5	1.031	1.177
	308	1.3826	64.1	1.028	1.065
	313	1.3813	62.7	1.025	0.930
DMF	293	1.3666	64.8	0.981	0.949
	298	1.3654	63.3	0.978	0.859
	303	1.3641	61.8	0.976	0.783
	308	1.3627	60.4	0.973	0.717
	313	1.3613	59.0	0.971	0.662
FM	293	1.3917	96.3	1.068	2.414
	298	1.3906	94.3	1.065	2.129
	303	1.3892	92.4	1.062	1.887
	308	1.3879	90.6	1.059	1.678
	313	1.3865	88.7	1.056	1.497

^aSolvent mixture = 30:70% (v/v) mixture of H₂O and respective solvent.

Effect of method selected

Three different methods (Gileadi²⁵, Nicholson^{22,23} and Kochi²⁴) have been used to evaluate k_{exp}^o values for reduction processes in bipyridinium monocations. By comparing the values of k_{exp}^o obtained from these methods for MV at different temperatures (Table 2) and all other compounds at 298 K (Table 3) it is observed that these results are similar at a lower temperature range (293-305 K). However, as the temperature increases the results obtained from Nicholson deviate from the results obtained from 2 other methods. The experimental results show that k_{exp}^o evaluated at a different temperature from that in Gileadi's and Kochi's methods are closer to each other compared to the k_{exp}^o values obtained from Nicholson's method. Throughout this study the trend for k_{exp}^o values was observed as $k_{\text{Gild}}^o > k_{\text{Koch}}^o > k_{\text{Nich}}^o$. Comparison of ΔG_{exp}^* values for the MV⁺/MV process calculated by applying equation (5) (Table 4) and from the slope of the plot $-\ln k_{\text{exp}}^o T^{-1/2}$ vs. T^{-1} and from the slope of Arrhenius equation reveals that the values evaluated by applying Kochi's and Gileadi's methods are close to each other, compared to ΔG_{Nich}^* (Table 5).

It is obvious from the experimental results for standard heterogeneous rate constants for the viologen compound system (Tables 2 and 3) that there are smaller variations with temperature in the values of rate constants evaluated using Gileadi's method compared to the variation in the other two methods. This may be due to the fact that Gileadi's method considers only the variations in the cathodic peak with increasing

scan rates, while the other 2 methods consider both cathodic and anodic peaks for the calculation of k_{exp}^o values. Thus, the k_{exp}^o values obtained from Gileadi's method may be considered more reliable than those obtained from the other 2 methods.

Table 2. The experimental values of standard heterogeneous electron transfer rate constants (k_{exp}^o) for the process $\text{MV}^{+1} + \text{e}^- \rightarrow \text{MV}$.

Solvent Mixture	$k_{\text{exp}}^o \times 10^3 / \text{cm s}^{-1}$				
	Temp./ K				
	293	298	303	308	313
DMSO	0.72 ± 0.01	0.97 ± 0.01	1.27 ± 0.01	01.67 ± 0.02	02.27 ± 0.06^G
	2.25 ± 0.14	3.90 ± 0.06	7.40 ± 0.20	13.80 ± 0.08	43.80 ± 0.20^N
	1.90 ± 0.15	2.70 ± 0.50	4.00 ± 0.98	05.80 ± 1.20	08.60 ± 1.80^K
DMF	0.86 ± 0.01	1.26 ± 0.02	1.68 ± 0.03	02.30 ± 0.06	03.00 ± 0.07^G
	2.77 ± 0.07	4.22 ± 0.08	7.60 ± 0.06	14.90 ± 0.12	61.70 ± 4.00^N
	2.80 ± 0.07	3.70 ± 0.10	5.40 ± 0.27	06.90 ± 0.50	09.90 ± 0.30^K

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

Table 3. The experimental values of standard heterogeneous electron transfer rate constants k_{exp}^o at 298 K.

Solvent Mixture	$k_{\text{exp}}^o \times 10^3 / \text{cm s}^{-1}$			
	MV ⁺ /MV	DQ ⁺ / DQ	BV ⁺ /BV	NBV ⁺ /NBV
DMSO	0.97 ± 0.01	0.57 ± 0.003	01.0 ± 0.03	0.80 ± 0.020
	3.90 ± 0.06	2.40 ± 0.030	04.6 ± 0.10	1.70 ± 0.007
	2.70 ± 0.50	2.00 ± 0.280	03.3 ± 0.60	1.60 ± 0.090
DMF	1.26 ± 0.02	0.71 ± 0.002	01.8 ± 0.13	0.90 ± 0.020
	4.22 ± 0.08	5.86 ± 0.040	10.1 ± 0.02	9.50 ± 0.020
	3.70 ± 0.10	4.00 ± 1.000	04.0 ± 0.50	4.70 ± 1.000
FM	-	-	19.3 ± 0.30	-
	-	-	12.0 ± 1.70	7.79 ± 1.700
	-	-	01.0 ± 0.03	-

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

ΔG_{exp}^* and ΔH_{exp}^* values for the MV^+ / MV system obtained from the Arrhenius and thermodynamic equation (Table 4) also show the same pattern. A similar trend was observed in all the 4 experimental viologen reductions in different solvent mixtures. This means the Gileadi and Kochi approaches are closer to each other compared to Nicholson. However, at comparatively low temperatures the results from all the methods approach are close to each other. Moreover, Nicholson's method is confined to low scan rates (due to limiting values of ψ), while Gileadi and Kochi are applicable to a much wider range of scan rates.

Effect of solvent

In the present work mixtures of 3 different solvents with water were employed. It was observed that the values for k_{exp}^o in the 3 solvent mixtures are in order of $k_{\text{FM}}^o > k_{\text{DMF}}^o > k_{\text{DMSO}}^o$ (Table 3). The highest

value of k_{exp}^o is expected for the FM mixture as it is more polar and has highest values of dielectric constant compared to the DMF and DMSO mixtures (Table 1).

Table 4. The experimental values of change in standard free energy of activation (ΔG_{exp}^*) for the process $\text{MV}^{+1} + e^- \rightarrow \text{MV}$.

Solvent mixture	$\Delta G_{\text{exp}}^* \times 10 / (\text{eV})$				
	Temp./ K				
	293	298	303	308	313
DMSO	3.96 ± 0.010	3.95 ± 0.009	3.95 ± 0.008	3.94 ± 0.009	3.93 ± 0.010^G
	3.67 ± 0.020	3.59 ± 0.010	3.50 ± 0.010	3.40 ± 0.007	3.13 ± 0.017^N
	3.71 ± 0.020	3.69 ± 0.050	3.65 ± 0.060	3.62 ± 0.058	3.57 ± 0.059^K
DMF	3.90 ± 0.009	3.88 ± 0.010	3.87 ± 0.010	3.86 ± 0.010	3.85 ± 0.010^G
	3.62 ± 0.012	3.57 ± 0.010	3.50 ± 0.008	3.36 ± 0.007	3.04 ± 0.020^N
	3.62 ± 0.013	3.61 ± 0.013	3.57 ± 0.018	3.57 ± 0.020	3.53 ± 0.010^K

ΔG_{exp}^* is calculated using the equation $k_{\text{exp}}^o = Z_{\text{het}} \exp(-\Delta G_{\text{exp}}^*/k_B T)$.

Table 5. The experimental values of change in standard free energy of activation ΔG_{exp}^* for the process $\text{MV}^{+1} + e^- \rightarrow \text{MV}$.

Solvent mixture	$^a \Delta G_{\text{exp}}^* \times 10 / (\text{eV})$			$^b \Delta G_{\text{exp}}^* \times 10 / (\text{eV})$		
	Gileadi	Nicholson	Kochi	Gileadi	Nicholson	Kochi
DMSO	4.3	11.2	5.8	4.5	11.4	5.9
DMF	4.8	11.6	4.9	4.9	11.8	5.0

(a) ΔG_{exp}^* is evaluated from the slope by plotting $-\ln k_{\text{exp}}^o T^{-1/2}$ vs. T^{-1} .

(b) ΔG_{exp}^* is evaluated from the slope of the Arrhenius equation.

It has been reported that reactants interact with the solvent polarization mode²⁸. In general, a solvent of high polarity will favor electron transfer and the rate of the electron transfer reaction is controlled by the polarity and dielectric constant of the solvent^{29,30}.

As the Z-values are a measure of polarity, it is reported that a solvent with a high Z-value would exhibit large values of k_{exp}^o ^{31,32}. Z-values for the solvent mixtures used are in the order of $Z_{\text{FM}} > Z_{\text{DMF}} \approx Z_{\text{DMSO}}$, which obviously justifies the highest values of k_{FM}^o ; the higher values of k_{DMF}^o compared to k_{DMSO}^o will be discussed later.

Moreover, in solvents with high Z-values, highly packed more stable ion pairs of solvent and solute are formed and less reactant species may be available for dimerization and more reactant species may be available for charge transfer. Thus, in solvents with high Z-values larger values of k_{exp}^o are expected to be obtained. Generally, throughout the experimental work, k_{exp}^o shows the highest values in the FM mixture, which can be justified on the basis of the high dielectric constant, high dipole moment and high Z-values of the FM mixture compared to the DMF and DMSO mixtures. However, higher values of k_{DMF}^o compared to k_{DMSO}^o cannot be explained on the basis of these criteria.

To explain this anomaly the effect of viscosity should be taken into account. Viscosity can affect the rate of diffusion of reactive species, which in turn affects the rate of electron transfer directly. As the DMSO mixture is more viscous than the DMF mixture (Table 1), the rate of diffusion should be slower in DMSO and hence the rate constant should be smaller. From the comparison of k_{exp}^o it can be inferred that the viscosity effect may dominate in DMF and DMSO mixtures, whereas in the FM mixture dielectric constant, dipole moment and Z-value have a more pronounced effect.

It may be suggested that adsorption of ion-solvent pairs on the surface of the electrode may be favored in the DMF mixture rather than in the DMSO mixture. It can also be assumed that the DMSO mixture offers more resistance (greater i-R drop) compared to the DMF mixture because aprotic solvents offer more i-R drop than water³³ and the DMSO mixture contains a greater molar ratio of aprotic solvent (0.37) compared to the DMF mixture (0.35), thus explaining the higher rates of electron transfer in the DMF mixture than in the DMSO mixture. A similar pattern of k_{exp}^o has been reported in the literature in FM, DMF and DMSO³⁴.

The solvents FM, DMF and DMSO in pure state have dipole moments of 3.25, 3.82 and 4.3 Debye and their molecular weights are 45.04, 73 and 78 g/mol, respectively. Thus they show an association with water to form associated solvent particles of larger size in the order of DMSO > DMF > FM. According to the bulkiness of the ion-solvent pair in these solvents due to the molecular weight and associated particle sizes of the solvent their diffusion coefficients may be in the reverse order. Hence the maximum association of DMSO with water and a minimum value of diffusion coefficient of the electroactive species lead to the slowest relaxation, thus resulting in minimum values of k_{exp}^o in the DMSO mixture. The maximum values of k_{exp}^o in the FM mixture and intermediate in the DMF mixture are in agreement with the above criteria.

Anomalous Behavior of Cations in the FM Mixture at the Pt. Disk Electrode From Table 3 the difference in the behavior of NBV⁺¹, BV⁺¹, DQ⁺¹ and MV⁺¹ at the Pt. disk in the FM mixture may be due to the size of the side chain attached to the bipyridinium core. Cations having small side chains such as methyl viologen and diquat may diffuse faster and so get reduced at the rate that cannot be coped with at the applied range of scan rate (0.05 to 500 Vs⁻¹). However, species having larger side chains such as NBV⁺¹, the reduction peak can be observed at higher scan rates, and in the case of the molecule bearing a bigger side chain (such as BV⁺¹), and hence having slow diffusion, reduction is recorded even at slow scan rates. The absence of reduction peaks of MV⁺¹ and DQ⁺¹ in FM could not be explained.

Effect of Temperature

It was observed from the experimental results that the rate constants for electron transfer reactions of the viologens (k_{exp}^o) increase with the increase in temperature irrespective of the nature of the salt, solvent system and working electrode used (Table 2). This is in agreement with the trends reported in the literature³⁶ and with the theoretical results (Table 7). It is assumed that the electron transfer in the present study is diffusion controlled (as the effect of migration current was overcome by using a high concentration of supporting electrolyte). It is suggested that an increase in temperature increases the kinetic energy of the radical cations, which in turn increases the mass controlled diffusion rate of the reactive species. This suggestion is in agreement with the work reported in the literature³⁷. An increase in temperature decreases the potential barrier height^{38,39}, which results in an increase in k_{exp}^o values. The values of ΔG_{exp}^* (Tables 4 and 5) indicate that the potential energy barrier decreases with the increase in temperature.

Effect of side chain

The viologens under study differ in the length of the side chain attached to the bipyridinium core. Their chain length increases in the order of DQ \approx MV; NBV ; BV. It has been reported that the reorganizational barrier energy decreases⁴⁰ and the electroactivity of viologens increases⁴¹ with the increase in the chain length attached. However, unfortunately experimental values of the rate constants for heterogeneous electron transfer for dications and monocations of the viologens show no regular pattern, except for benzyl viologen, which shows the highest values of rate constants in all solvents for both reductions at both the electrodes. It has been reported^{40,41} that the side chain affects the values of rate constants in a similar way as observed in benzyl viologen. The viologens can also show self-electron exchange (proportionation and disproportionation) and the rate of electron self-exchange reaction increases with the decrease in the size of reactant⁴². Benzyl viologen is the biggest viologen in the present case, thus showing minimum self-exchange of electrons and maximum species is available for heterogeneous exchange of electrons at the surface of the electrode, thus showing maximum values of rate constants for heterogeneous electron transfer.

Activation parameters

Calculated and Graphical Values of Change in Free Energy of Activation ΔG_{exp}^* Values of ΔG_{exp}^* were calculated using the equation $k_{exp}^o = Z_{het} \exp(-\Delta G_{exp}^*/k_B T)$ (Table 4) and evaluated from the slope by plotting $-\ln k_{exp}^o T^{-1/2}$ vs. T^{-1} and from the slope of the Arrhenius equation (Table 5). The plots can be seen in Figure 3. As shown in Table 4, with the increase in temperature ΔG_{exp}^* values decrease and k_{exp}^o increases. This means temperature decreases the free energy of activation, resulting in a decrease in the energy barrier for the transfer of electrons at the surface of the electrode.

The values of ΔG_{exp}^* are also evaluated from the slope of the Arrhenius equation. These results are comparable with the results obtained from the slope by plotting $-\ln k_{exp}^o T^{-1/2}$ vs. T^{-1} (Table 5). As The 2 methods gave results in agreement with each other for both the reduction processes for all the 4 alkyl viologens in 3 solvent mixtures at 2 working electrodes, thus confirming the observed results. As all other viologen compounds show similar trends, only the results of MV are given in Table 2.

Change in Enthalpy of Activation (ΔH^*) and Entropy of Activation (ΔS^*) The values of ΔH^* and ΔS^* were calculated by applying the thermodynamic equation $\Delta H^* = \Delta G^* + T\Delta S^*$. Results obtained in the case of MV⁺ (Table 6) show that the entropy changes in electron transfer processes of the experimental bipyridinium halides in all solvent mixtures were quite small, and so no significant difference was observed between their ΔH_{exp}^* and ΔG_{exp}^* values. A similar trend is observed for other viologen compounds.

Theoretical Calculations of Rate Constant (k_{the}^o) Effect of Barrier Crossing Activation Parameter and Frequency Factor on k_{the}^o In this work we report the values of theoretical rate constants calculated using Marcus' equation (6) and a combination of equations (12), (13) and (14). A better agreement between the results for experimental rate constants and that of the theoretical one for the same system is observed when k_{el} in equation (6) is replaced by the barrier crossing activation energy parameter (κ) and distance of the electrode from the reaction site (δ) is also included. This replacement also includes the effect of the nature of the working electrode used. This suggests that for the electrochemical outer sphere electron transfer reactions, transmission coefficient (k_{el}) may not be necessarily equal to unity and the reaction may not be adiabatic in nature.

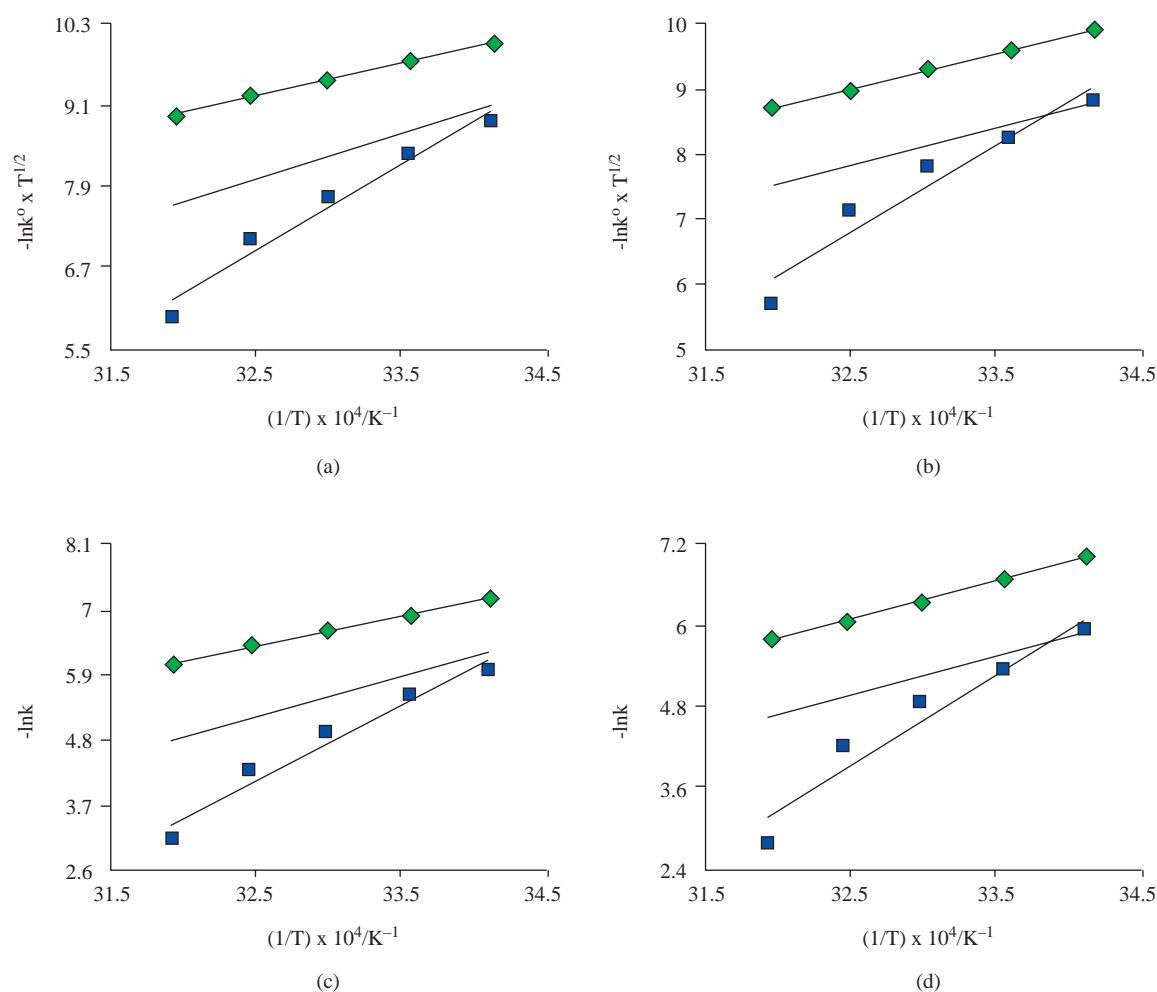


Figure 3. (a) $-\ln k^o T^{1/2}$ vs. $1/T$ for MV^{+}/MV at the Pt disk in DMSO mixture (b) $-\ln k^o T^{1/2}$ vs. $1/T$ for MV^{+}/MV at the Pt disk in DMF mixture (c) $-\ln k^o$ vs. $1/T$ for MV^{+}/MV at the Pt disk in DMSO mixture (d) $-\ln k^o$ vs. $1/T$ for MV^{+}/MV at the Pt disk in DMF mixture. \blacklozenge , \blacksquare , and \blacktriangle represent the results calculated using the Gileadi, Nicholson and Kochi methods.

Table 6. The experimental values of activation parameters for the process $MV^{+1} + e^{-} \rightarrow MV$ determined from the plots of ΔG_{exp}^* vs. T .

Solvent mixture	$\Delta S_{\text{exp}}^{o*} \times 10/ (\text{eV})$			$\Delta H_{\text{exp}}^* \times 10/ (\text{eV})$		
	Gileadi	Nicholson	Kochi	Gileadi	Nicholson	Kochi
DMSO	0.001	0.025	0.007	4.3	11.3	5.8
DMF	0.003	0.027	0.004	4.8	11.8	4.9

Excellent agreement can be achieved if the modified theoretical expression of the standard rate constant equation (12) is used in combination with equation (13) to include the dielectric and dynamic aspects of the solvent in the pre-exponential factors (the electronic transmission coefficient κ and the frequency factor ν_n) (Table 7) for the effect of ν_n on k_{the}^o values for reduction processes of cations of methyl viologen. Comparison of k_{the}^o with k_{exp}^o for reduction process of 4 experimental viologens at a Pt disk as the working

electrode gave results of the same pattern as discussed earlier (for MV). It is therefore important to point out that kinetic data in different solvents can be interpreted in terms of contemporary electron transfer theory^{40,43}, when the latter is modified to take into account the solvent dependence of the pre-exponential transmission coefficient and frequency factor in the rate expression.

Table 7. Theoretical heterogeneous electron transfer rate constant for MV⁺/ MV effect of ν_n on k_{the}^o ^{a,b}.

Solvent mixture ^l	$k_{the}^o \times 10^6 / (\text{cm.s}^{-1})$				
	Temp./ K				
	293	298	303	308	313
DMSO ⁱ	29.62	36.81	45.62	56.53	70.36 ^c
	185.4	230.46	285.68	354.17	440.99 ^d
	1178.19	1465.3	1817.48	2254.58	2809.05 ^e
	3007.01	3741.22	4642.45	5761.59	7181.87 ^f
	7796.24	9704.94	12050.26	14964.67	18665.78 ^g
	20780.27	25888.43	32174.84	39994.86	49935.84 ^h
DMF ⁱ	44.48	55.1	67.92	83.26	98.17 ^c
	280	347.02	427.97	524.82	619.07 ^d
	1796.15	2227.34	2748.72	3373.13	3981.67 ^e
	4616.43	5727.24	7071.34	8682.19	10254.03 ^f
	12087.38	15005.32	18539.8	22779.85	26924.35 ^g
	32704.3	40638.58	50264.95	61830.3	73165.09 ^h
DMSO ^j	118.89	144.41	174.97	212.03	259.61 ^c
	743.99	904.01	1095.74	1328.3	1627.09 ^d
	4728.01	5747.87	6971.08	8455.81	10364.30 ^e
	12066.99	14675.49	17806.49	21608.82	26498.31 ^f
	31285.9	38069.06	46219.74	56124.96	68869.51 ^g
	83390.18	101551.2	123409.1	150000.6	184243.93 ^h
DMF ^j	186	225.11	271.15	324.78	376.53 ^c
	1170.96	1417.72	1708.4	2047.19	2374.47 ^d
	7511.37	9099.71	10972.58	13157.58	15271.87 ^e
	19305.61	23398.35	28228.05	33866.71	39329.74 ^f
	50548.66	61303.48	74008.94	88857.57	103269.45 ^g
	136767.3	166026.9	200652.4	241182	280627.70 ^h
DMSO ^k	7.41	9.42	11.93	15.11	19.11 ^c
	46.37	58.95	74.7	94.68	119.80 ^d
	294.69	374.8	475.26	602.71	763.10 ^e
	752.12	956.95	1213.97	1540.21	1951.02 ^f
	1950.02	2482.38	3151.06	4000.42	5070.73 ^g
	5197.63	6621.87	8413.5	10691.61	13565.54 ^h
DMF ^k	10.68	13.53	17.07	21.4	25.66 ^c
	67.22	85.24	107.55	134.92	161.80 ^d
	431.19	547.12	690.75	867.15	1040.68 ^e
	1108.24	1406.84	1777.03	2231.98	2680.07 ^f
	2901.76	3685.91	4659.05	5856.13	7037.15 ^g
	7851.18	9982.47	12631.58	15895.03	19122.97 ^h

(a) For k_{the}^o see equation (12) & (12) (b) Pt disk electrode (c) $\delta = 0.85$ nm (d) $\delta = 0.75$ nm (e) $\delta = 0.65$ nm (f) $\delta = 0.60$ nm (g) $\delta = 0.55$ nm (h) $\delta = 0.5$ nm (i) $Re = 2(r+L)$, (j) $Re = 2r$, (k) $Re = \infty$ (l) solvent mixture = 30:70% (v/v) mixture of H₂O and respective solvent.

Comparison of k_{exp}^o and k_{the}^o The effect of the solvent mixture on k_{exp}^o and k_{the}^o is clear from Table 8. To justify this anomaly we should take into account the interaction of aprotic solvent with water, due to which a change in relaxation time may occur. Results from the FM mixture show fast relaxation while those from DMSO show slow relaxation, as expected from theory. It is reported³⁶ that solvent relaxation has inverse relation with k^o . In the case of DMSO and DMF, there may be a stronger association with water as compared to FM. The dipole moments of DMSO, DMF and FM are 4.3, 3.82 and 3.25, respectively; their association with water is expected to be in the following order, DMSO > DMF > FM, thus slowing relaxation in the same order.

Table 8. Comparisons of values of experimental and theoretical rate constants at 298 K.

Monocation of viologen	Results from	$k^o \times 10^3 / \text{cm.s}^{-1}$		
		DMSO mixture	DMF mixture	FM mixture
MV ⁺	Experiment	0.97 ± 0.010	1.26 ± 0.020	-
	Theory	$0.96^{c,e}$	$1.40^{c,e}$	-
DQ ⁺	Experiment	0.57 ± 0.003	0.71 ± 0.002	-
	Theory	$0.61^{a,d}$	$0.70^{b,f}$	-
BV ⁺	Experiment	1.00 ± 0.030	1.80 ± 0.130	19.3 ± 0.300^N
	Theory	$1.40^{a,g}$	$2.30^{a,g}$	$19.9^{c,d}$
NBV ⁺	Experiment	0.80 ± 0.020	0.90 ± 0.020	7.70 ± 1.700^K
	Theory	$0.74^{a,g}$	$1.16^{a,g}$	$8.70^{c,d}$

(a) $\text{Re} = 2(r+L)$ (b) $\text{Re} = 2r$ (c) $\text{Re} = \infty$ (d) $\delta = 0.5 \text{ nm}$ (e) $\delta = 0.55 \text{ nm}$ (f) $\delta = 0.6 \text{ nm}$ (g) $\delta = 0.65 \text{ nm}$ (h) $\delta = 0.75 \text{ nm}$ (i) mixture of water with respective solvent in 30:70% v/v results obtained by applying the Gileadi equation are reported above except in 2 cases, where these are not available; thus in these 2 cases experimental values of rate constant by using (N) Nicholson and (K) Kochi are reported.

A study of the effect of side chain, a comparison of theoretical results for 4 experimental viologens (which differ in length of side chain), showed the following trend $\text{BV} > \text{NBV} > \text{MV} > \text{DQ}$ for rates of successive heterogeneous transfer of electrons. While values of their experimental rate constants (except in the case of benzyl viologen) do not follow any regular trend. In the case of benzyl viologen there was no contradiction between the theoretical and experimental pattern. The anomaly between the trends of k_{exp}^o and k_{the}^o in the case of the remaining 3 viologens needs further investigation.

Conclusion

The results obtained can be summarized as follows. The experimental values of heterogeneous electron transfer rate constants (k_{exp}^o) obtained by Gileadi's method are more reliable as they show less variation and this method incorporates E_p values obtained at all applied scan rates. k_{exp}^o values were affected by the nature of the solvents and temperature. In solvents of higher polarity higher rate constants were observed. An increase in temperature increases the kinetic energy of the ion-solvent pair and hence increases the diffusion rate, which results in higher values of k_{exp}^o . The electroactivity of species is also a direct result of the size of the side chain attached to the viologen's core. The BV gives the highest rate constant value

due to having the biggest side chain, while the other 3 viologens do not differ in this respect to a significant extent. Therefore, no regular trend was observed.

Theoretical values of heterogeneous electron transfer rate constants (k_{the}^o) calculated by taking into account the work term, the barrier crossing energy of activation and nuclear frequency factor and with a modification $\lambda_i = 0$ hence $\nu_o = 0$ and $\nu_n = \nu_o$ gave the best agreement between the theoretical and experimental data. Thus it is concluded that inner reorganization energy (neglected in this work) may not affect the reactivity of selected viologens to an appreciable extent.

Abbreviations Used

k^o Heterogeneous electron transfer rate constant

k_{exp}^o Experimental rate constant for heterogeneous electron transfer process

k_{The}^o Theoretical rate constant for heterogeneous electron transfer process

Pt disk Platinum disk

MV⁺¹ Methyl viologen monocation

V⁺¹ Viologen monocation

NBV⁺¹ n-Butyl viologen monocation

BV⁺¹ Benzyl viologen monocation

BQ⁺¹ Diquat monocation

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