# TRANSFER OF 1,1'-DIALKYL-4,4'-BIPYRIDINIUM DICATION (VIOLOGEN) ACROSS THE WATER–DICHLOROETHANE AND WATER–NITROBENZENE INTERFACES

Josef HANZLÍK and Zdeněk SAMEC

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10-Hostivař*

Transfer of viologen dications $R_2V^{2+}$ (R = methyl, ethyl, propyl, butyl, pentyl, heptyl or benzyl) across the water–1,2-dichloroethane and water–nitrobenzene interfaces has been studied by cyclic voltammetry. Effects of the changes in the viologen structure and in the composition of solutions of both phases on the voltammetric behaviour have been inspected. Ion association, in particular that occuring in the organic phase, has a considerable influence on the viologen dication transfer and plays the key role in the proposed charge transfer mechanism. From the conductivity measurements the association constants for viologen tetraphenylborates in nitrobenzene have been evaluated. From the voltammetric measurements the Gibbs energies of transfer of viologen dications across the water–nitrobenzene interface have been determined.

Viologens have permanently attracted a great deal of interest evoked by their physico--chemical (and in particular the oxidation-reduction) properties. The herbicide effect of viologens ("paraquat family") has been discovered earlier[1] and its close relation to the redox properties has been evidenced[2].

At present the viologen redox system is being used as one of the links (or mediators) in redox chains of both the homogeneous[3] and the heterogenous[4] model systems, which should serve for the solar-to-electric energy conversion. In these cases viologens play the role of so-called relay or trapping compounds, consisting in that viologen as a reversible redox couple ensures the total charge separation through the electron transfer from a photosensitive redox couple to a suitable acceptor. Viologens have also been used for the modification of the electrode surfaces[5] and their practical utilization in electrochromic display devices has been attempted. Electrochemical behaviour of viologens has been reviewed by Bird and Kuhn[6].

The present paper follows our previous communication[7], where the use of viologens for the charge separation at the interface between two immiscible electrolyte solutions has been suggested. Here the main attention will be given to the transfer of viologen dications across the water–organic solvent interface and to its correlation with structure of the molecule.

## EXPERIMENTAL

### Chemicals

Symmetric viologens $R_2V^{2+}$ were prepared as described in literature[8]. Tetraphenylborates of viologens were prepared from the corresponding bromides by their precipitation with sodium tetraphenylborate (*puriss. p.a.*, Fluka AG) in water. For the preparation of the non-aqueous phase *puriss. p.a.* grade 1,2-dichloroethane (DCE) and nitrobenzene (NB) supplied from Fluka AG were used as received. Prior to the conductivity measurements nitrobenzene was distilled from a mixture with the activated aluminium oxide under the pressure of $0.7-1 \cdot 10^3$ Pa at a very low rate. Lithium bromide (*puriss. p.a.*, Fluka AG), tetrabutylammonium bromide — TBABr
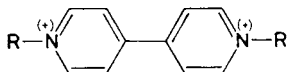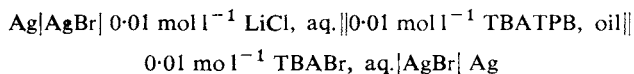


| | |
|---|---|
| *I*, R = CH$_3$ | *V*, R = (CH$_2$)$_4$CH$_3$ |
| *II*, R = CH$_2$CH$_3$ | *VI*, R = (CH$_2$)$_6$CH$_3$ |
| *III*, R = (CH$_2$)$_2$CH$_3$ | *VII*, R = C$_6$H$_5$ |
| *IV*, R = (CH$_2$)$_3$CH$_3$ | |

(*puriss. p.a.*, Fluka AG), tetrabutylammonium tetraphenylborate — TBATPB prepared as described in literature[9], and tetrabutylammonium 3,3'-*como*-bis(undecahydro-1,2-dicarba-3-cobalta--*closo*-dodecabor)ate (1-) — TBADCC prepared in the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences (Řež near Prague), were used as base electrolytes.

### Apparatus

Electrolytic cell for cyclic voltammetry[10] as well as the scheme of the electronic circuit[11] have been described previously. The interface between the aqueous and the non-aqueous phase established in the cell had an area of $31.4$ mm$^2$. The potential difference $E$ of the electrochemical cell

$$\text{Ag}|\text{AgBr}|\,0.01\text{ mol l}^{-1}\text{ LiCl, aq.}\|0.01\text{ mol l}^{-1}\text{ TBATPB, oil}\|$$

$$0.01\text{ mol l}^{-1}\text{ TBABr, aq.}|\text{AgBr}|\text{ Ag}$$

was controlled by means of a four-electrode potentiostat[11] with an automatic ohmic potential drop compensation. $E$ is the Galvani potential difference $\Delta_o^w\varphi = \varphi(w) - \varphi(o)$ between the aqueous and the non-aqueous phase, which is related to the formal potential difference for the tetrabutylammonium cation $\Delta_o^w\varphi_{TBA^+}^0$: $E = \Delta_o^w\varphi - \Delta_o^w\varphi_{TBA^+}^0$ (ref.[11]). The value $\Delta_o^w\varphi_{TBA^+}^0 = -0.275$ V (ref.[13]) was calculated from the extraction data. The range of potentials within which a charge transfer can be measured is cut off by the transfer of tetrabutylammonium ion at negative potentials and by the transfer of tetraphenylborate ion at positive potentials (Fig. 1, curve *1*).

## RESULTS AND DISCUSSION

Viologens, which were prepared as solids in the form of bromides, were dissolved in the aqueous phase together with the base electrolyte. With the increasing number

of sweeps during the multi-sweep cyclic voltammetry the drop in the current was observed without showing a tendency to a steady-state, which points to irreversible changes in the interface. Therefore, only the single-sweep voltammograms were recorded.

A typical cyclic voltammogram of the viologen dication transfer across the water–organic solvent interface is shown in Fig. 1. The positive and negative peak currents, corresponding to the charge transfer from the aqueous to the non-aqueous phase and the reverse, respectively, have an equal height, which increases linearly with the square root of the polarization rate and with the viologen concentration in the aqueous phase $(5 \cdot 10^{-5} - 2 \cdot 10^{-3} \text{ mol l}^{-1})$, cf. Fig. 2.

The peak potential $E_p$ is independent of both the polarization rate $(5 - 100 \text{ mV s}^{-1})$ and the viologen concentration. Under the conditions of experiment the peak potential difference $\Delta E_p$ is constant and equals to $29 \pm 2$ mV. Nernstian slope for $n = 2$ (i.e. $2 \cdot 303 \, RT/zF$) can be obtained from the logarithmic analysis of the convolution integral[15].

All the viologens studied show an analogous voltammetric behaviour. The experimental data obtained fit in the Randles–Ševčík equation and based on the theory of cyclic voltammetry[14] a conclusion can be drawn, that a diffusion-controlled charge
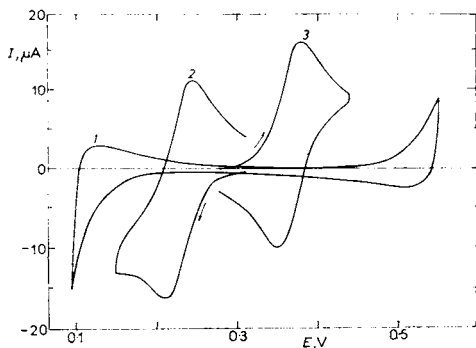
FIG. 1

Cyclic voltammograms $(20 \text{ mV s}^{-1})$ of the charge transfer across the water–dichloroethane interface for: 1 base electrolyte; 2 benzylviologen; 3 methylviologen. Composition of the aqueous phase: $0 \cdot 01 \text{ mol l}^{-1}$ LiBr $+ 2 \cdot 10^{-4} \text{ mol l}^{-1}$ viologen; dichoroethane: $0 \cdot 01 \text{ mol l}^{-1}$ TBADCC. Initial potential of the single sweep: 2 330 mV or 3 280 mV. Direction of polarization is indicated by arrow
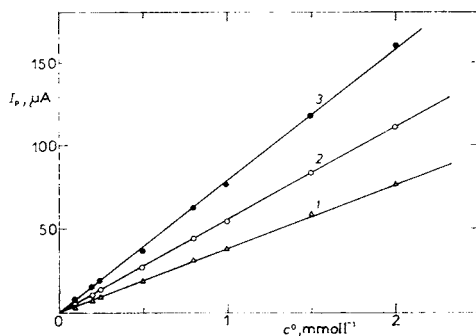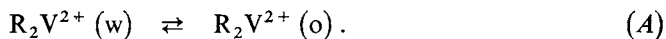
FIG. 2

Plot of the current peak height $I_p$ vs concentration of methylviologen in the aqueous phase at various polarization rates $v$ (mV s$^{-1}$) 1 5; 2 10, and 3 20

transfer reaction across the water–organic solvent interface takes place, which can be described by Eq. $(A)$.

$$R_2V^{2+}(w) \rightleftarrows R_2V^{2+}(o).\tag{A}$$

From the experimental values of $E_p$ the half-wave potentials $E_{1/2}^{rev}$ were calculated according to the relationship

$$E_p - E_{1/2}^{rev} = -1 \cdot 109\,(RT/zF)\tag{1}$$

*cf.* Table I. Obviously, $E_{1/2}^{rev}$ depends strongly on the size of the substituent R. A linear plot of $E_{1/2}^{rev}$ *vs* the reciprocal molecular radius (estimated from a model) or *vs* the effective length of R, which is given by the number of carbon atoms in the chain, conforms to the Born equation.

The extension of the side chain R results in an increase of the molecular dimensions, which in turn has a direct effect on the diffusion coefficient of the ion in water $D^w$; *cf.* Table II for its values estimated from the voltammetric measurements. With the increasing number of carbon atoms in the chain R a shift of $E_{1/2}^{rev}$ towards the less positive potentials is apparent, and also in the same sequence the hydrophobic character of the particle $R_2V^{2+}$ becomes more pronounced. (The case for R = $C_6H_5$ in water–nitrobenzene system has already no visible voltammetric response). As it can be seen from Table I, the ion transfer to the polar NB $(\varepsilon^{298} = 34 \cdot 82)$ is more favourable energetically than that to the less polar DCE $(\varepsilon^{298} = 10 \cdot 23)$. The differences in $E_{1/2}^{rev}$ in the presence of either TPB$^-$ or DCC$^-$ anion are rather small in NB, but they reach up to 80 mV in DCE. This reflects an increased influence of the base electrolyte anion on the charge transfer, which is higher in the less polar medium.

In cases, for which the simple ion transfer has been proved unambiguously, the values of the standard Galvani potential difference $E^0$ can be obtained from Eq. $(2)$

$$E_{1/2}^{rev} = E^0 + \left(\frac{RT}{2zF}\right)\ln\left(\frac{D_i^w}{D_i^o}\right)\tag{2}$$

and these can be used further for the evaluation of the Gibbs energies of ion transfer. With respect to the experimental conditions applied in voltammetry at the interface between two immiscible electrolyte solutions (ITIES), the simple ion transfer is rather unique phenomenon. The system contains a number of ions arising by dissociation from the base electrolyte or from the substance studied and interacting with each other. Since in any case one of the solvent phases has the dielectric permittivity lower than 40, it is predicted by the Bjerrum theory[23] that these interactions will be strong and the ion association will complicate the transfer of the ion studied across the interface[16].

In the case of viologens a remarkable tendency to aggregation has been observed[17] as well as the strong interaction of dication with various anions, which eventually leads to an electron transfer between the anion and the cation and to the formation of the charge-transfer complex[18].

Thus the ion-pair formation in the organic phase presumably influence to an increased extent the transfer of the viologen dication, while that in the aqueous phase

TABLE I
Half-wave potentials $E_{1/2}^{rev}$ for the viologen dication transfer across the water–dichloroethane and water–nitrobenzene interfaces in the presence of TBATPB and TBADCC as base electrolytes in the organic phase. Viologen concentration $2\cdot5 . 10^{-4}$ mol $l^{-1}$, $0\cdot01$ mol $l^{-1}$ LiBr in water

| Viologen $R_2V^{2+}$ | $E_{1/2}^{rev}$, V (DCE) | | $E_{1/2}^{rev}$, V (NB) | |
|---|---|---|---|---|
| | $0\cdot01$ mol $l^{-1}$ TBATPB | $0\cdot01$ mol $l^{-1}$ TBADCC | $0\cdot01$ mol $l^{-1}$ TBATPB | $0\cdot01$ mol $l^{-1}$ TBADCC |
| I | 0·297 | 0·363 | 0·273 | 0·280 |
| II | 0·270 | 0·352 | 0·247 | 0·254 |
| III | 0·236 | 0·320 | 0·218 | 0·228 |
| IV | 0·197 | 0·257 | 0·188 | 0·164 |
| V | 0·160 | 0·220 | 0·157 | 0·146 |
| VI | 0·165 | 0·225 | 0·148 | 0·156 |
| VII | 0·093 | 0·148 | — | — |

TABLE II
Diffusion coefficients $D^w$ of viologens in the aqueous phase, association constants $K_a(R_2VTPB)$ for the parameter $a = 0\cdot6$ nm, formal Galvani potentials $\Delta_{NB}^w\varphi_{R_2V^{2+}}^0$ and corresponding Gibbs energies $\Delta G_{tr,R_2V^{2+}}^{0,w\to NB}$ for the viologen dication transfer from the aqueous to nitrobenzene phase; w: $1 . 10^{-2}$ mol $l^{-1}$ LiBr + $2\cdot5 . 10^{-4}$ mol $l^{-1}$ $R_2V^{2+}$, o: $1 . 10^{-2}$ mol $l^{-1}$ TBATPB

| Viologen $R_2V^{2+}$ | $D^w . 10^6$ cm$^2$ s$^{-1}$ | $K_a$ mol$^{-1}$ l | $\Delta_{NB}^w\varphi_{R_2V^{2+}}^0$ V | $\Delta G_{tr,R_2V^{2+}}^{0,w\to NB}$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| I | 4·54 | 580 | 0·019 | 3·66 |
| II | 3·10 | 648 | —0·006 | —1·15 |
| III | 2·30 | 677 | —0·037 | —7·14 |
| IV | 2·27 | 649 | —0·065 | —12·54 |
| V | 1·50 | 608 | —0·097 | —18·72 |
| VI | 0·87 | 632 | —0·105 | —20·26 |
| VII | 0·44 | — | — | — |

can be neglected. The overall mechanism of the viologen dication transfer is shown by the Scheme 1.
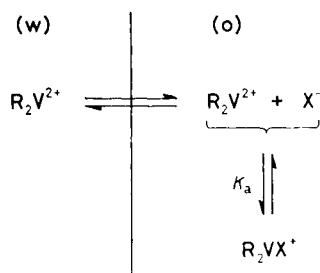


SCHEME 1

For the sake of simplicity the successive formation of the ion pairs has been neglected. This mechanism was verified experimentally through the correlation of the reversible half-wave potential $E_{1/2}^{rev}$ with the concentration of the base electrolyte anion in the organic phase. The plot of $E_{1/2}^{rev}$ vs ln $c^{\circ}$ ($c^{\circ}$ is the analytical concentration of TBATPB or TBADCC) is a straight line with a negative slope close to $(3/2)(RT/F)$ for both solvents ($cf.$ Fig. 3). At the concentration of the base electrolyte in the organic phase lower than 0·01 mol $l^{-1}$ the slope of the plot changes towards positive values. (Owing to experimental reasons this correlation was not verified at concentrations lower than 0·005 mol $l^{-1}$, in which cases the ohmic resistance became rather considerable and could not be compensated safely). The effect of the change in the base
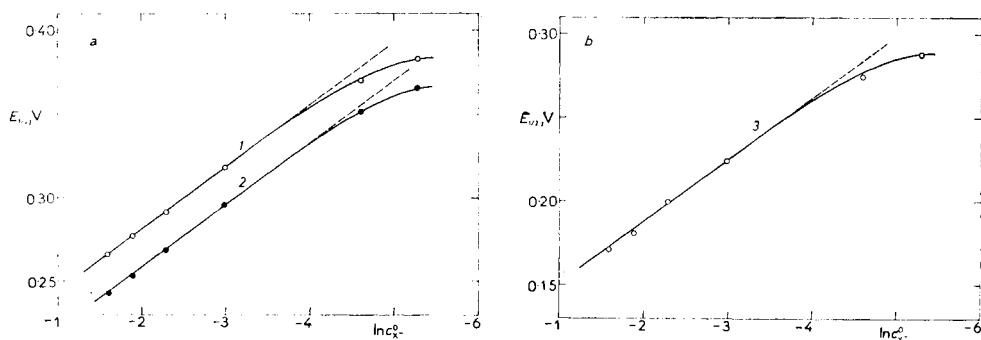


FIG. 3

Plot of $E_{1/2}^{rev}$ vs concentration of the base electrolyte in the organic phase for the transfer of the viologen $R_2V^{2+}$ ($c = 2·5 . 10^{-4}$ mol $l^{-1}$). $a$ $1$ $Me_2V^{2+}$, TBATPB in NB; $2$ $Et_2V^{2+}$, TBATPB in DCE; $b$ $Et_2V^{2+}$, TBADCC in DCE

electrolyte concentration in the organic phase on the value of $E_{1/2}^{rev}$ for the viologen dication transfer has two reasons. First of all the change in the TBA$^+$ concentration in the organic phase results in a change in the equilibrium Nernst–Donnan potential at the water–organic solvent interface. For concentrations $c_{TBA^+}^o > c_{TBA^+}^w$ this dependence has a negative slope close to $(RT/F)$ (after the correction for the association in NB, which is small[19]). Following the mechanistic scheme suggested for the ion transfer coupled to the ion association, an equation can be derived for $E_{1/2}^{rev}$ which is quite analogous to that known from the classical polarography for the reversible reduction of metal complexes, namely[20]

$$E_{1/2}^{rev} = E^0 + \left(\frac{RT}{2F}\right) \ln \frac{(D_i^w)^{1/2}}{(D_i^o)^{1/2}(1 + K_a c^o)} . \tag{3}$$

Consequently, the contribution ot the resulting slope of $E_{1/2}^{rev}$ $vs$ $\ln c^o$ arising from the specific type of the ion transfer mechanism has the value close to $-(RT/2F)$ at $K_a \gg 1$.

The net variation of $E_{1/2}^{rev}$ is a superposition of both contributions. The change in the slope at $c_{TBA^+}^o < c_{TBA^+}^w$ reflects the inversion in the sign of the equilibrium Nernst––Donnan potential. Using the Fuoss–Justice equation[21], a rough estimate of the association constant $K_a$ was made on the basis of the conductivity measurements[12] performed with the TBATPB solutions in dry nitrobenzene. The calculated values of the association constants are given in Table II.

The values of $K_a$ so obtained may not fit in Eq. (3), because in contrast to the conductivity measurements, the voltammetry was not carried out with dry nitrobenzene, but with nitrobenzene saturated with water. Moreover, the algorithm for the evaluation of $K_a$ according to the theory of the electrolytic conductance in case of non--symmetric electrolytes is not available[22]. The values of $K_a$ are of the same order of magnitude for all the viologens, small differences being insignificant with respect to the change in the molecular structure.

From Eq. (3) the formal Galvani potentials were evaluated for the viologen dication transfer from water to nitrobenzene saturated with water, and are summarized in Table II together with the corresponding values of the Gibbs energy of transfer. These data will be used in selecting the viologen derivative suitable for the photoelectrochemical measurements at the ITIES.

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