
**TRANSFER OF TRISBIPYRIDINE TRANSITION METAL COMPLEXES
ACROSS THE WATER-DICHLOROETHANE INTERFACE**Josef HANZLÍK^a, Jan HOVORKA^a and Anna Maria CAMUS^b^a *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 102 00 Prague 10-Hostivař, Czechoslovakia and*^b *Dipartimento di Scienze Chimiche, Università di Trieste, 341 27 Trieste, Italia*

Received April 23rd, 1986

Transfer of trisbipyridine transition metal complexes $[M(\text{bpy})_3]^{2+}$ (bpy = bipyridine) across the water-1,2-dichloroethane interface can be classified as a simple transfer of a divalent cation in case that the central atom $M = \text{Fe, Ni, Ru}$ or Os , while for $M = \text{Co, Cu}$ or Zn the charge transfer is accompanied by considerable chemical changes, such as the ligand dissociation and the solvolysis. Thermodynamic and transport parameters characterizing the transfer of $[M(\text{bpy})_3]^{2+}$ ions from water to 1,2-dichloroethane have been determined from voltametric measurements.

Trisbipyridine transition metal complexes and their structural analogs represent a distinct class of compounds, the remarkable oxidation-reduction properties of which are particularly interesting¹. Electrochemical studies in non-aqueous media provide valuable information on electron transfer reactions, as well as evidence for the formation of bipyridine complexes in less-common oxidation states^{2,3}. A series of such complexes with the central metal atom being in a low oxidation state have actually been prepared⁴. Bipyridine complexes have enjoyed a broad application in catalysis as efficient mediators of the electron transfer^{5,6}. In this respect, the exploitation of bipyridine complexes⁷ and their analogs⁸ in the solar-to-chemical energy conversion⁹ appears to be rather attractive.

On the other hand, the electron transfer between two nonmetallic phases can be encountered in various branches of chemistry, *cf.* the photoinitiated reactions in micelles¹⁰ or the electron transfer across biological or artificial membranes¹¹. Also in these cases, bipyridine complexes have been used either as mediators or photo-sensitizers of the electron transfer, eventually immobilized in redox polymers¹².

Electrochemical measurements of the electron transfer across the interface between two immiscible electrolyte solutions can yield information on kinetics and mechanism of the transfer. This makes it possible to understand the role of the electron transfer in more complex processes, *e.g.* in the photoinduced interfacial charge separation. However the only direct evidence for the electron transfer has been so far available for the system of ferrocene in nitrobenzene and hexacyanoferrate(III) in water¹³. As mentioned earlier¹⁴, the electron transfer between photoexcited tris(2,2'-bipyridine)-

Ru(II) and alkyl-viologen across the water-1,2-dichloroethane interface appears to be worth considering.

This study was performed in order to obtain basic information on charge transfer processes at the water-1,2-dichloroethane interface in the presence of trisbipyridine transition metal complexes, which could be used in designing the system with the electron transfer across the interface between two immiscible electrolyte solutions.

EXPERIMENTAL

Chemicals

Chloride salts of trisbipyridine metal complexes were prepared according to procedures described in literature (Fe¹⁵, Ru¹⁶, Os¹⁷, Co, Cu, Zn¹⁸, Ni¹⁹). Their composition was checked by chemical analysis, the results of which were satisfactory. In order to prevent its oxidation in the air, this cobalt complex was prepared using the Schlenk flask technique²⁰. Copper and zinc complexes were not recrystallized, inasmuch they split off readily one ligand either during heating of their aqueous solution or in the presence of anorganic polar solvent.

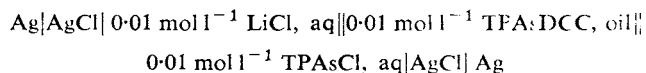
Tetraphenylborates were prepared by addition of a small excess of the concentrated aqueous solution of sodium tetraphenylborate to the aqueous solution of sulphate (or iodide in case of osmium²¹) of the corresponding trisbipyridine complex. Nickel complex gives the powder, which can be recrystallized from hot dichloroethane. The other products give a fine suspensions, which were separated by centrifugation, washed with water several times and dried in vacuum. These complexes, when recrystallized from acetone, form the crystals, which contain one or two solvent molecules.

Complexes of cobalt, copper, and zinc containing less than three bipyridine ligands in the molecule were prepared from trisbipyridine particles, as recommended in literature²².

1,2-dichloroethane (*puriss. p.a.*, Fluka AG) was used as received. The aqueous solutions were prepared from the re-distilled water. Lithium chloride and tetraphenylarsonium chloride (TPAsCl) or tetraphenylarsonium dicarbollylcobaltate(III) (TPAsDCC) — for the preparation see ref.²³, were used as the base electrolytes for the aqueous or the organic solvent phase, respectively.

Apparatus

Voltammetric measurements were performed in an all-glass four-electrode cell^{24,25}, where the water-organic solvent interface having an area of 20.42 mm² was established. The potential difference E of the galvanic cell



was measured, which was the Galvani potential difference between the aqueous (w) and the non-aqueous (o) phase defined as $\Delta_o^w\phi = \phi(w) - \phi(o)$, related to the formal potential difference for tetraphenylarsonium cation $\Delta_o^w\phi_{\text{TPAs}^+}^0$, i.e. $E = \Delta_o^w\phi - \Delta_o^w\phi_{\text{TPAs}^+}^0$. The value $\Delta_o^w\phi_{\text{TPAs}^+}^0 = 0.364 \text{ V}$ was obtained from the extraction data²⁶. The potential range, within which a charge transfer reaction can be measured, is cut off by the transfer of tetraphenylarsonium cation or dicarbollylcobaltate(III) anion at negative or positive potentials, respectively. The ions studied are transferred at rather negative potentials and, in order to avoid the interference with the transfer

of the base electrolyte ions, the tetraphenylarsonium salt was preferred over the tetrabutylammonium salt when choosing the base electrolyte. In fact, $\Delta_o^w \varphi_{\text{TPAs}^+}^0$ is by 139 mV more negative than $\Delta_o^w \varphi_{\text{TBA}^+}^0$ (cf. ref.²⁶) and, consequently, the presence of tetraphenylarsonium cation results in an expansion of the potential *window* towards negative potentials.

All experiments were performed at a temperature of 25°C with the solutions prepared in the air. UV-VIS spectra were taken on the Specord M40 Spectrometer (Zeiss, Jena).

RESULTS AND DISCUSSION

Chloride salts of trisbipyridine transition metal complexes, with the central atoms Fe, Ru, Os, Co, Ni, Cu or Zn being in the oxidation state +II, were dissolved in the aqueous solution containing 0.01 mol l^{-1} LiCl as a base electrolyte. The transfer of the complex divalent cation $[\text{M}(\text{bpy})_3]^{2+}$ (M or bpy denotes the central atom or bipyridine molecule, respectively) from water to 1,2-dichloroethane was studied by cyclic voltammetry. All experimental data were obtained from single-sweep voltammograms. As it has been shown earlier²⁷, the ion transfer across the interface between two immiscible electrolyte solutions can be described by the same equations as in the case of the electron transfer across the metal–electrolyte solution interface. Since the shape of the voltammetric curve reflects the mechanism and kinetics of the charge transfer, a formally analogous voltammetric behaviour indicates an analogous mechanism. On the basis of their voltammetric behaviour the complexes studied can be divided into two groups.

Transfer of Complex Cations Trisbipyridine Fe(II), Ru(II), Os(II), and Ni(II)

A typical voltammogram of the $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer across the water–1,2-dichloroethane interface is shown in Fig. 1. The peak height I_p^+ for the ion transfer from

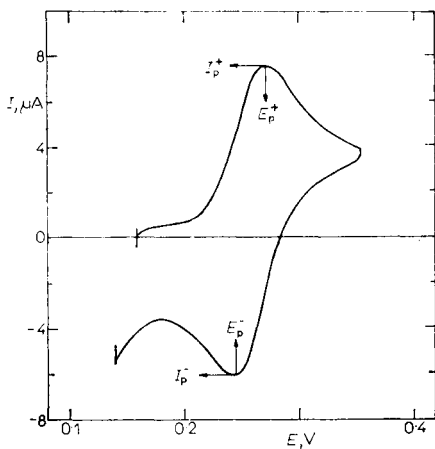
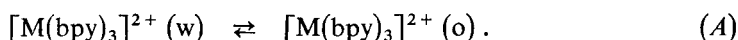


FIG. 1

Cyclic voltammogram of $[\text{Fe}(\text{bpy})_3]\text{Cl}_2 \cdot v = 20 \text{ mV s}^{-1}$, initial potential $E_1 = 0.160 \text{ V}$, single sweep; w: 0.01 mol l^{-1} LiCl, $1 \cdot 10^{-4} \text{ mol l}^{-1}$ $[\text{Fe}(\text{bpy})_3]\text{Cl}_2$; o: 0.01 mol l^{-1} TPAsDCC in 1,2-dichloroethane

water to 1,2-dichloroethane is proportional to the concentration of the complex compound ($1 \cdot 10^{-4} - 5 \cdot 10^{-3} \text{ mol l}^{-1}$). The dependence of I_p^+ on the square root of the polarization rate v ($5 - 100 \text{ mV s}^{-1}$) is linear and crosses the origin of coordinates. The peak height I_p^- for the ion transfer from 1,2-dichloroethane to water equals to I_p^+ . The peak potentials E_p^+ and E_p^- do not depend either on the concentration of the complex or on the polarization rate. Their difference $\Delta E_p = E_p^+ - E_p^-$ is close to 29 mV. Both the peak current I_p and the peak potential E_p are not influenced by bipyridine added to the solution of the complex compound up to the bipyridine concentration 0.1 mol l^{-1} .

These experimental data indicate that the behaviour of the system is analogous to the reversible electron transfer reaction²⁸. In the present case, the diffusion-controlled charge transfer across the water-1,2-dichloroethane interface proceeds according to the equation



The reversible half-wave potential $E_{1/2}^{\text{rev}}$ has been calculated from the equation

$$E_p^+ = E_{1/2}^{\text{rev}} - 1.109 (RT/zF) \quad (1)$$

and the formal potential E^0 from the equation

$$E_{1/2}^{\text{rev}} = E^0 + (RT/2zF) \ln (D_w/D_o). \quad (2)$$

No remarkable effect of the ion-pair formation, which would facilitate the ion transfer was detected experimentally. Consequently, this step was not considered in the overall reaction scheme.

The Randles-Ševčík voltammetric behaviour implies that the diffusion coefficient of the ion $[\text{M}(\text{bpy})_3]^{2+}$ in water, D_w , can be evaluated from the equation

$$I_p^+ = 2.687 \cdot 10^8 \cdot AD_w^{1/2} v^{1/2} c_w^0. \quad (3)$$

On the basis of the Stokes theory, the diffusion coefficient of the particle in the organic phase has been estimated from the ratio of the viscosity coefficients of both solvents and the value of D_w .

The value of the formal potential E^0 is closely related to the formal Galvani potential difference $\Delta_o^w \varphi_{\text{compl}}^0$ (the subscript "compl" denotes the complex cation $[\text{M}(\text{bpy})_3]^{2+}$). The latter quantity can be evaluated from the equation

$$E^0 = \Delta_o^w \varphi_{\text{compl}}^0 - \Delta_o^w \varphi_{\text{ref}}^0 \quad (4)$$

provided that the formal Galvani potential difference $\Delta_{\circ}^w \varphi_{\text{ref}}^0$ for the reference ion (here tetraphenylarsonium) is known. Table I summarizes reversible half-wave potentials $E_{1/2}^{\text{rev}}$, formal Galvani potential differences $\Delta_{\circ}^w \varphi_{\text{comp1}}^0$, diffusion coefficients D_w and Gibbs energies $\Delta G_{\text{comp1}}^{0, w \rightarrow o}$ for $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer from water to 1,2-dichloroethane calculated from the equation

$$\Delta_{\circ}^w \varphi_{\text{comp1}}^0 = \Delta G_{\text{comp1}}^{0, w \rightarrow o} / 2F. \quad (5)$$

The change in the apparent Gibbs energy for $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer from water to 1,2-dichloroethane reflects mainly changes in solvation energies during process of the ion resolution. Since the transferred complexes are highly symmetric particles, which are rather inert to the substitution ($E_{1/2}$ does not depend on the concentration of the free ligand), the contribution to $\Delta G_{\text{comp1}}^{0, w \rightarrow o}$ arising from the change in the ion structure can be neglected. Due to the increase in volume of the particle, which is connected with the replacement of the central atom in a sequence from Fe to Os, its diffusion coefficient decreases and hydrophobic character becomes more pronounced.

Transfer of Complex Cations Trisbipyridine Co(II), Cu(II), and Zn(II)

Voltammogram recorded for a freshly prepared aqueous solution of trisbipyridine Co(II) chloride is shown in Fig. 2 (curve 1). Two pairs of the considerably unsymmetric peaks appear on the voltammogram. The well-developed peak, belonging to the pair of peaks at more negative potentials, corresponds to the charge transfer from the organic solvent to water, but the ratio $I_p^+ / I_p^- < 1$. Plot of the peak height I_p^- vs the square root of the polarization rate v is a straight line, which crosses the ori-

TABLE I

Thermodynamic and transport constants for the $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{Ni}$) from water to 1,2-dichloroethane, 0.01 mol l^{-1} LiCl and $1 \cdot 10^{-4} \text{ mol l}^{-1}$ $[\text{M}(\text{bpy})_3]^{2+}$ in water, 0.01 mol l^{-1} PTAsDCC in 1,2-dichloroethane

Complex ion	$E_{1/2}^{\text{rev}}, \text{V}$	$\Delta_{\circ}^w \varphi_{\text{comp1}}^0, \text{V}$	$D_w \cdot 10^6, \text{cm}^2 \text{s}^{-1}$	$\Delta G_{\text{tr, comp1}}^{0, w \rightarrow o}, \text{kJ mol}^{-1}$
$[\text{Fe}(\text{bpy})_3]^{2+}$	0.256	-0.106	2.66	-20.45
$[\text{Ru}(\text{bpy})_3]^{2+}$	0.248	-0.115	2.51	-22.19
$[\text{Os}(\text{bpy})_3]^{2+}$	0.243	-0.119	2.32	-22.96
$[\text{Ni}(\text{bpy})_3]^{2+}$	0.260	-0.102	2.47	-19.68

gine of coordinates. The peak potential E_p^- shifts towards more negative values when v increases. The peak potential difference ΔE_p is close to 30 mV.

The peak height I_p^+ for the charge transfer from the aqueous to the non-aqueous phase is not influenced by the change in the reverse potential E_λ , but $I_p^+/v^{1/2}$ increases with v . These experimental data point to considerable chemical changes, which complicate the charge transfer itself.

In order to eliminate the possibility that the complex had already been decomposed during the preparation of the solid phase, this preparation was repeated several times in the atmosphere of an inert gas, which should prevent the oxidation of the solution, by the air oxygen. However, all the samples showed the same voltammetric behaviour.

Since I^+ is not influenced by E_λ , the chemical change is obviously very fast and occurs in time interval, which is much shorter than the duration of the voltammetric sweep.

Fig. 2 (curve 1) illustrates that another couple of peaks appears at more positive potentials. The negative current, which corresponds to the charge transfer from the organic to the aqueous phase, is very low and even merges in the base electrolyte current. The high I_p^+ of the broad peak, which is obviously a superposition of two overlapping peaks, is less than one half of I_p^- in the former couple of peaks. The same voltammogram were obtained irrespective of whether the complex compound was dissolved in water or in dichloroethane. In order to demonstrate that the couple of

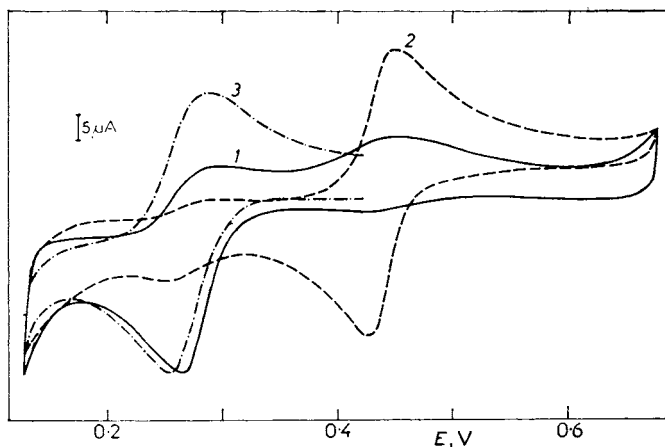


FIG. 2

Cyclic voltammogram of $[\text{Co}(\text{bpy})_3]\text{Cl}_2$. $v = 50 \text{ mV s}^{-1}$, multisweep; w: 0.01 mol l^{-1} LiCl, $5 \cdot 10^{-4} \text{ mol l}^{-1}$ $[\text{Co}(\text{bpy})_3]\text{Cl}_2$; o: 0.01 mol l^{-1} TPAsDCC in 1,2-dichloroethane. 1 freshly prepared solution; 2 solution after three days standing in the air; 3 fresh solution with an addition of 2,2'-bipyridine (0.01 mol l^{-1}) to the aqueous phase

peaks at more positive potentials is due to the products of complex dissociation, the transfer of complexes with a less number of ligands in molecule was also measured, the particle transferred being $[\text{Co}(\text{bpy})_2]^{2+}$ or $[\text{Co}(\text{bpy})]^{2+}$. Their voltammograms were alike but, in contrast to the voltammogram of $[\text{Co}(\text{bpy})_3]^{2+}$, the exhibited only couple of peaks at more positive potentials.

It is known that the stability of $[\text{M}(\text{bpy})_3]^{2+}$ in the aqueous solution decreases on both increasing or decreasing the solution pH (ref.³²). When hydroxide ions are present in the aqueous phase, no current connected with the charge transfer from water to organic phase is apparent on the voltammogram. This fact can be explained in terms of the formation of the conjugated base, which is subsequently reduced and the products are transferred outside the available potential range. The presence of hydroxonium cation results in an increase of the positive current in the potential range, where the transfer of $[\text{Co}(\text{bpy})_2]^{2+}$ can be expected to occur. Here, however, the protonized form of bipyridine released from the complex can be also partitioned, so that the two processes overlap.

The course of the cyclic voltammogram on the branch corresponding to the charge transfer back from dichloroethane to water reflects mainly the effect of drop in dielectric constant of medium on complex formation³³. In dichloroethane the complex equilibrium is shifted in favour of the particle $[\text{Co}(\text{bpy})_3]^{2+}$, giving rise to the peak I_p^- of the peak couple at more negative potentials.

On addition of the free ligand-2,2'-bipyridine – to the aqueous solution of the complex, couple of peaks at more positive potentials diminishes and even disappears when the concentration ratio $[\text{bipyridine}]/[\text{complex}] > 1$, whereas the peak I_p^+ of the first peak couple increases and E_p^+ shifts towards more negative potentials (cf. Fig. 2, curve 3). It is apparent from Fig. 3 that when concentration of the free ligand exceeds considerably that of the complex, $[\text{bipyridine}]/[\text{complex}] > 10^2$, the ratio $I_p^+/I_p^- = 1$ and ΔE_p being independent of v is close to 29 mV.

From all these experimental data a conclusion can be drawn that the transfer of the $[\text{Co}(\text{bpy})_3]^{2+}$ cation across the water–1,2-dichloroethane is complicated by a change in the chemical structure of the basic complex, namely by the dissociation of the ligand. Its splitting off results in the formation of particles with lower coordination numbers. UV-VIS spectra of these solutions reveal the presence of the free ligand with absorption bands at 280.1 and 232.9 nm (cf. ref.³⁰). Equilibrium is shifted in favour of the product of dissociation. Known values of the consecutive stability constants for complexes of $\text{Co}^{2+}(\text{Ar}/3d^7s$ with the electronic configuration $t_{2g}^6 e_g^1$ (ref.³¹)) point to a lower stability of the particle with the coordination number six, as compared with the particle having the coordination number four.

The results presented above were obtained with freshly prepared solutions. Cyclic voltammograms of the same solutions, but measured a few days later, were completely different (cf. Fig. 2, curve 2). A rest of couple of peaks at more negative is still seen, but 200 mV more positively a couple of peaks appears for which the ratio $I_p^+/I_p^- = 1$

and $\Delta E_p = 28$ mV, independently of v . Experimental plots correspond to the simple transfer of a divalent particle. Since formally the charge number is not changed, it can be assumed that the latter couple of peaks is due to the product of solvolysis, *i.e.* the particle $[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$.

TABLE II

Thermodynamic and transport constants for the $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer ($\text{M} = \text{Co}, \text{Cu}, \text{Zn}$) from water to 1,2-dichloroethane, 0.2 mol l^{-1} 2,2'-bipyridine, 0.01 mol l^{-1} LiCl and $1 \cdot 10^{-4} \text{ mol l}^{-1}$ $[\text{M}(\text{bpy})_3]\text{Cl}_2$ in water, 0.01 mol l^{-1} TPAsDCC in 1,2-dichloroethane

Complex ion	$E_{1/2}^{\text{rev}}, \text{V}$	$\Delta \phi_{\text{comp}}^{\text{w} \rightarrow \text{o}}, \text{V}$	$D_w \cdot 10^6, \text{cm}^2 \text{s}^{-1}$	$\Delta G_{\text{tr,comp}}^{\text{o,w} \rightarrow \text{o}}, \text{kJ mol}^{-1}$
$[\text{Co}(\text{bpy})_3]^{2+}$	0.255	-0.107	2.91	-20.65
$[\text{Cu}(\text{bpy})_3]^{2+}$	0.263	-0.099	2.25	-19.10
$[\text{Zn}(\text{bpy})_3]^{2+}$	0.267	-0.095	3.51	-18.33

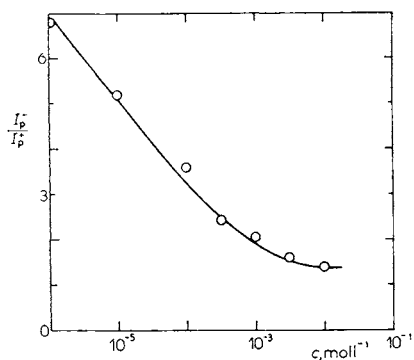


FIG. 3

Plot of the peak height ratio *vs* concentration of free 2,2'-bipyridine in the aqueous phase for the $[\text{Co}(\text{bpy})_3]^{2+}$ ion transfer across the water-1,2-dichloroethane interface

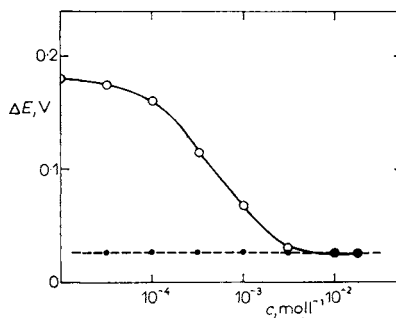
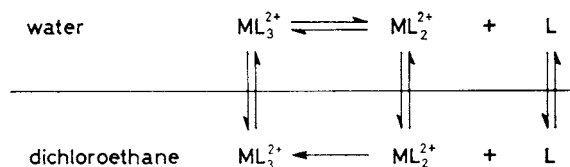


FIG. 4

Plot of the peak potential difference $\Delta E_p = E_p^+ - E_p^-$ *vs* concentration of free 2,2'-bipyridine in the aqueous phase for the $[\text{Zn}(\text{bpy})_3]^{2+}$ ion transfer across the water-1,2-dichloroethane interface. O transfer of $[\text{Zn}(\text{bpy})_3]\text{Cl}_2$; ● transfer of $[\text{M}(\text{bpy})_3]\text{Cl}_2$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{Ni}$)

Mechanism of the $[\text{Co}(\text{bpy})_3]^{2+}$ ion transfer across the water-dichloroethane interface can be described by the Scheme 1.



SCHEME 1

The interfacial region, where the ion transfer from water to dichloroethane takes place, is considerably diffuse. The system is in equilibrium and the boundary has the character of a mixed solvent layer. Towards each of the bulk solutions, the portion of the other solvent molecules decreases. It is evident, that in course of the $[\text{Co}(\text{bpy})_3]^{2+}$ ion transfer from the freshly prepared solutions, water molecules do not enter the coordination sphere of the complex. In fact, the aquatic reaction was not detected in the time scale of experiment. Moreover, it can be assumed, that the change in the coordination number connected with the ligand dissociation will induce the isomerization reactions leading to an increase of the complex stability and thereby preventing the coordination of solvent.

Trisbipyridine copper and zinc complexes exhibit a similar voltammetric behaviour, for which the appearance of the couple of well-developed peaks on the voltammogram is characteristic with the ratio $I_p^+/I_p^- = 1$. In these cases, however, the peak height is lower than one half of that corresponding to the simple divalent ion transfer. The peak potential difference depends strongly on rate of change of the applied voltage and reaches for rather high values ($\Delta E_p = 180 \text{ mV}$ at $v = 100 \text{ mV s}^{-1}$ in case of $[\text{Zn}(\text{bpy})_3]^{2+}$), *cf.* Fig. 4. Transfer reactions of mono- and bisbipyridine copper complexes occur in the range of more positive potentials, where they interfere with the transfer of base electrolyte ions. As a result only an enhancement of the base electrolyte current can be observed here. On the other hand, all available zinc complexes, $[\text{Zn}(\text{bpy})_2]\text{Cl}_2$ and $[(\text{ZnCl}_2)(\text{bpy})_3]$, do not practically differ in voltammetric behaviour from $[\text{Zn}(\text{bpy})_3]^{2+}$. Although in solid phase these compounds are chemically defined, it has to be assumed that through consecutive equilibria a series of zinc complexes appears in the aqueous solution, from which only $[\text{Zn}(\text{bpy})_3]^{2+}$ is transferred within the potential range available. Its transfer kinetics is influenced by complex equilibrium under the lack of ligand.

Standard Gibbs energies for the $[\text{M}(\text{bpy})_3]^{2+}$ ion transfer from water to 1,2-dichloroethane in presence of the free 2,2-bipyridine are given in Tables I and II.

One of us (A. C.) thanks the Italian MPI for financial support.

REFERENCES

1. McWhinnie W. R., Miller J. D.: *Adv. Inorg. Chem. Radiochem.* **12**, 135 (1969).
2. Saji T., Aoyagui S.: *J. Electroanal. Chem. Interfacial Electrochem.* **58**, 401 (1975).
3. Ohsawa Y., DeArmond M. K., Hanck K. W., Morris D. E.: *J. Am. Chem. Soc.* **105**, 6522 (1983).
4. Herzog S., Taube R.: *Z. Anorg. Allg. Chem.* **306**, 160 (1960).
5. Oyama N., Anson F. C.: *J. Electrochem. Soc.* **127**, 247 (1980).
6. Bontempelli G.: *Ann. Chim. (Rome)* **75**, 19 (1985).
7. Kalyasundaram K.: *Coord. Chem. Rev.* **46**, 159 (1982).
8. Rillema D. P., Allen G., Meyer T. J., Conrad D.: *Inorg. Chem.* **22**, 1617 (1983).
9. Grätzel M.: *Acc. Chem. Res.* **14**, 376 (1981).
10. Fendler J. H.: *Catalysis in Micellar and Macromolecular Systems*. Academic Press, New York 1975.
11. Jortner J.: *Biochim. Biophys. Acta* **594**, 193 (1980).
12. Leidner C. R., Murray R. W.: *J. Am. Chem. Soc.* **106**, 1606 (1984).
13. Samec Z., Mareček V., Weber J.: *J. Electroanal. Chem. Interfacial Electrochem.* **103**, 11 (1979).
14. Samec Z., Homolka D., Mareček V., Kavan L.: *J. Electroanal. Chem. Interfacial Electrochem.* **145**, 213 (1983).
15. Inskeep R. G.: *J. Inorg. Nucl. Chem.* **24**, 763 (1962).
16. Palmer R. A., Piper T. S.: *Inorg. Chem.* **5**, 864 (1966).
17. Burstall F. H., Dwyer F. P., Gyrfas E. C.: *J. Chem. Soc.* 953 (1950).
18. Jaeger F. M., Van Dijk J. A.: *Z. Anorg. Allg. Chem.* **227**, 273 (1936).
19. Schweitzer G. K., Lee J. M.: *J. Phys. Chem.* **56**, 195 (1952).
20. Herzog S., Dehnert J.: *Z. Chem.* **4**, 1 (1964).
21. Cook M. J., Lewis A. P., McAuliffe S. G.: *Org. Magn. Reson.* **22**, 388 (1984).
22. Lee R. H., Griswood E., Kleinberg J.: *Inorg. Chem.* **3**, 1278 (1964).
23. Hawtorne M. F., Young D. C., Andrews T. D., Howe D. V., Pilling R. L., Pitts A. D., Reintjes M., Warren L. F., Wegner P. A.: *J. Am. Chem. Soc.* **90**, 879 (1968).
24. Samec Z., Mareček V., Weber J.: *J. Electroanal. Chem. Interfacial Electrochem.* **100**, 841 (1979).
25. Homolka D., Mareček V.: *J. Electroanal. Chem. Interfacial Electrochem.* **112**, 91 (1980).
26. Czapkiewicz J., Czapkiewicz-Tutaj B.: *J. Chem. Soc., Faraday Trans. 1*, **76**, 1663 (1980).
27. Samec Z.: *J. Electroanal. Chem. Interfacial Electrochem.* **99**, 197 (1979).
28. Bard A. J., Faulkner L. R.: *Electrochemical Methods*, p. 213. Wiley 1980.
29. Nicholson R. S., Shain I.: *Anal. Chem.* **36**, 706 (1964).
30. DeArmond M. K., Hill J. E.: *J. Chem. Phys.* **54**, 2247 (1971).
31. Irving H., Mellor D. P.: *J. Chem. Soc.* 1962, 5222.
32. Gillard R. D.: *Coord. Chem. Rev.* **16**, 67 (1975).
33. Fuoss R. M., Krauss C. A.: *J. Am. Chem. Soc.* **55**, 1019 (1933).

Translated by Z. Samec.