

SPECTROCOULOMETRY — A NEW SPECTRO-ELECTROCHEMICAL TECHNIQUEJán MOCÁK^a, Michal NÉMETH^a, Mieczysław L APKOWSKI^b and Jerzy W. STROJEK^b^a *Department of Analytical Chemistry,**Slovak Institute of Technology, 812 37 Bratislava, Czechoslovakia and*^b *Institute of Inorganic Chemistry and Technology,**Silesian Technical University, 44—100 Gliwice, Poland*

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A spectrocoulometric macrocell with a direct-view optical probe was designed and constructed, where the optical signal is transferred by light-conducting glass or quartz fibres permitting to work at wavelengths above 410 or 300 nm. The method of measurement on the proposed equipment is described; it was tested in the study of the mechanism and kinetics of oxidation of $\text{Fe}(\text{bipy})_3^{2+}$ ions (bipy = 2,2'-bipyridyl) with the use of potentiostatic coulometric electrolysis with open-circuit relaxation at a suitable time. The primary product of electrolysis, $\text{Fe}(\text{bipy})_3^{3+}$, undergoes a follow-up hydrolytic reaction with the formation of a binuclear complex. The rate constant of the reaction of the first order involves the contributions, k_{Bi_i} , from all bases present in solution; the corresponding values for H_2O , OH^- , bipy, and CH_3COO^- ions at a ionic strength 0.5 mol dm^{-3} and 25°C were determined as $k_{\text{OH}} = (5.0 \pm 0.6) \cdot 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_{\text{bipy}} = (1.3 \pm 0.2) \cdot 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_{\text{Ac}} = (5.8 \pm 1.0) \cdot 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and $k_{\text{H}_2\text{O}}$ is not significant with respect to experimental errors.

Spectroelectrochemistry has become a wide-spread research method in chemical laboratories during recent years. Its advantages and applications are known from several publications¹⁻³: it combines two different instrumental techniques and yields electrochemical and spectral data at the same time.

The spectroelectrochemical methods developed up to now involve one of the voltamperometrical techniques, hence changes in the spectrum take place in the diffusion or reaction layer at the working electrode. When optically transparent electrodes are used, the effective optical path corresponds to the thickness of the diffusion or reaction layer where the absorbing substance is non-uniformly distributed. This fact limits the applicability of the method to substances with a high molar absorption coefficient and complicates the mathematical analysis of the time dependence of absorbance. The concentration of the component under study is a function of the time and distance from the electrode and is given by the solution of a system of partial differential equations. Their usual nonlinearity makes an analytical solution impossible. The interpretation of results may be simplified if the electrochemical changes take place in the whole solution (coulometrical regime). The effective optical

length is then given by the dimension of the spectroelectrochemical cell along the optical axis, the concentrations are equal in the whole volume, and ordinary differential equations are adequate for the description.

The object of the present work is to show the advantages of combining potentiostatic coulometry and spectrophotometry to obtain a new method, spectrocoulometry.

EXPERIMENTAL

Chemicals and Solutions

2,2'-Bipyridyl of reagent grade was recrystallized from ethanol. Solutions of $\text{Fe}(\text{bipy})_3^{2+}$ ions (bipy = 2,2'-bipyridyl) were prepared by dissolving a weighed quantity of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ in a solution of 2,2'-bipyridyl; the concentration of the complex was $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ and the concentration of excess bipyridyl was chosen as desired. The pH of the solution was adjusted by adding KOH or HNO_3 (as in ref.⁴) or by an acetate buffer. The ionic strength was adjusted by adding KCl to $I = 2.0$ or 0.5 mol dm^{-3} . The auxiliary electrode space was filled with 1M-NaCl, the junction between this and the working electrode was filled with 1M- KNO_3 containing an agar gel. The salt bridge of the calomel reference electrode contained 4M-NaCl.

Spectrocoulometric Cell

The coulometric cell used earlier by us^{5,6} served as a base for the design of the spectrocoulometric cell, whose characteristic feature is that the optical signal is transferred by light-conducting fibres. This permits recording the spectral characteristics of the electrolysed solution while securing a rapid and selective electrolysis^{5,6}, *i.e.* effective stirring, uniform potential distribution at the working electrode, and simple, reproducible hydrodynamics. The body of the spectrocoulometric cell shown in Fig. 1 contains also the optical probe and a removable bottom; its other parts are identical to those of the high-efficiency coulometric cell described earlier^{5,6}. The opening 6 ending beside the cell bottom and serving as sample inlet was used to insert the light conductor into the space of the working electrode 1. The depth of insertion of the optical probe inlet 11 is controlled by means of Teflon distance rings 15. In their absence the probe is inserted as deep as the widened portion 12 permits, whereby a 5 mm optical path is defined. Optical paths from 5 to 30 mm can be adjusted by combining rings 1, 2, 5, 10, and 20 mm in height, whose position is delimited by the widened portion of the probe. The inlet portion of the probe, which serves to introduce the optical signal into the studied solution, consists of a Teflon cylinder closed by a lens 14 and containing the light-conducting cable 13 connected with a spectrophotometer. The optical signal passes through the solution and is led back into the spectrophotometer through the second part 16 of the optical probe; this consists of a light-conducting cable 13 inserted into a screwable Teflon cylinder terminated with a lens 14. The lens, which is 5 mm in diameter and has a 12 mm focus, serves to prevent contact of the light-conducting fibres with the studied solution and to focus the optical signal from the solution into the second light conductor, thus suppressing losses of light by dispersion. Other openings have the following purposes: 2 space for the salt bridge of the reference electrode separated by a porous carbon plate from the working space, 3 inlet of gas above the electrolysed solution, 4 inlet of inert gas into the space of the auxiliary electrode, 5 holding screws, 7 space for auxiliary electrode (from the outer side of the cell body), 8 openings joining the working and auxiliary electrode spaces (closed by a fine glass

frit held in place by a screwable ring), and 10 opening for a three-way stopcock serving for inlet of an inert gas into the analysed solution and for outlet of the solution.

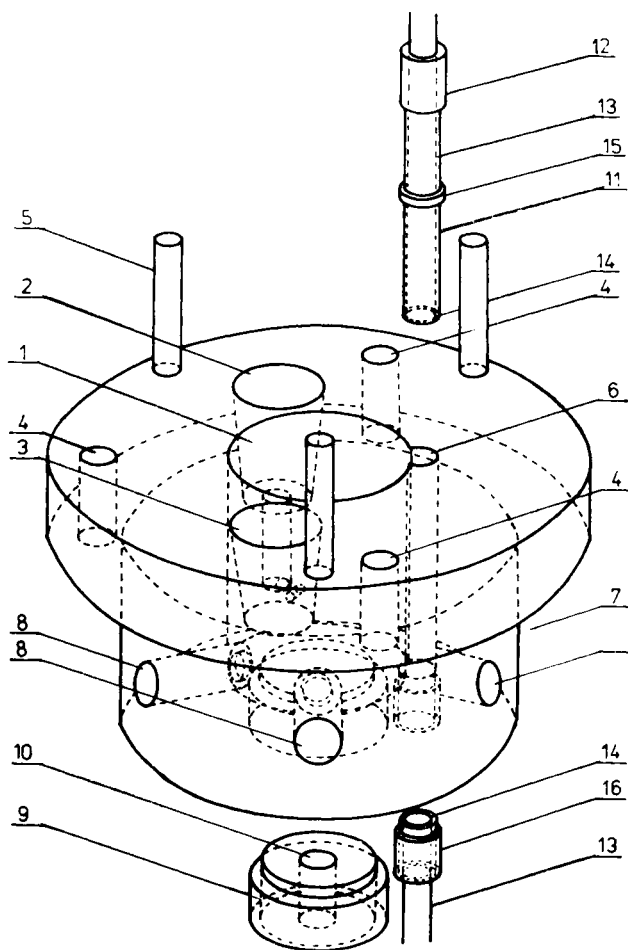


FIG. 1

Core of spectrocoulometric cell. 1 Working electrode space, 2 space for salt bridge of reference electrode; spaces 1 and 2 are separated by porous carbon; 3 inlet of inert gas above the electrolysed solution, 4 inert gas inlet into the auxiliary electrode space, 5 holding screws, 6 opening for introducing sample and inserting the inlet portion of the optical probe, 7 auxiliary electrode space, 8 openings joining the spaces 1 and 7, closed by a dense frit with a screwed Teflon ring, 9 Teflon bottom of the cell, 10 opening for a three-way stopcock serving for inlet of inert gas into the analysed solution and for outlet of the solution, 11 inlet portion of the optical probe, 12 widened portion of the optical probe, 13 light-conducting cable, 14 lens, 15 separating rings, 16 second part of the optical probe

The direct-view optical probe was made from a light-conducting glass cable of 5 mm diameter (Carl Zeiss, Jena) or from a quartz cable manufactured in our laboratory from quartz fibres supplied by the Department of Silicates, Prague Institute of Chemical Technology, Prague. With the glass cable, the spectral range is limited to wavelengths above 410 nm, whereas with the quartz cable the UV region down to about 300 nm can be employed.

Measuring System

The measuring system consisted of a standard coulometric accessory and a spectrophotometrical set-up. A universal electrochemical apparatus Mehrzweckpolarograph GWP 673 (Akademie der Wissenschaften, Berlin) served for coulometric measurements. The working electrode was a platinum net, the smaller one of a pair of Fischer electrodes, of a cylindrical shape, 30 mm in height 32 mm in diameter, and approximate geometrical area of 25 cm². Carbon rods bound with Pt wires served as auxiliary electrode, and a saturated calomel, electrodes is described elsewhere⁶.

Spectrophotometric measurements at constant wavelength were done on a Spekol 10 apparatus (Zeiss, Jena), however, another spectrophotometer can be used as well (Fig. 2). The use and possibilities of a very rapid measuring system (Rapid Scanning Mirror Spectrophotometer (RSS))⁷ permitting a record of a chosen part of a visible spectrum during electrolysis and controlled by a computer are described elsewhere⁸.

THEORETICAL

Coulometry at controlled potential is one of the analytical methods used in studying the kinetics and mechanism of chemical reactions coupled with the electrode process^{9,10}. Its disadvantage is that it permits to follow experimentally only the concentration changes of the electroactive compound (as the current-time dependence). The concentration changes of electroinactive compounds cannot be followed, although they can be simulated (on the assumption of a known mechanism and known values of parameters of the chemical reactions involved). The correctness of the proposed mechanism can be checked and the parameters calculated by comparing the time dependence of the measured current (usually in dimensionless form, I/I_0 ,

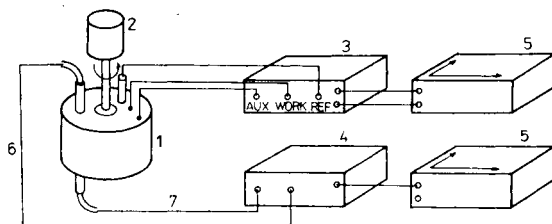


FIG. 2

Spectrocoulometric measuring system. 1 Spectrocoulometric cell, 2 equipment for the rotating electrode or stirrer, 3 potentiostat, 4 SPEKOL 10, 5 XY recorder, 6 input light-conducting cable, 7 output light-conducting cable

which is equal to the dimensionless concentration c/c_0 in the case of only one electro-active substance) with the simulated current course and minimizing the sum of squares of the deviations. However, the experimental data do not permit to judge the correctness of the simulated concentration–time dependence of electroinactive intermediates or products of a more complicated electrochemical process. This is possible in spectro-electrochemical methods, of which the best variant, as mentioned in the introduction, is that which combines coulometry with absorption spectroscopy. Such a bisensor (or, after addition of another optical probe, multisensor) analysis can be carried out with the apparatus described. The advantage comparing with hitherto known spectroelectrochemical methods is not only a long optical path and simplicity of mathematical description, but also the preparative character of the new method making it possible to isolate and to analyse the products of the electrochemical process, thus contributing substantially to the information content. Finally, if the electric circuit is disconnected at a chosen instant, it is possible to follow the sole chemical process and to apply the methods of chemical kinetics.

RESULTS AND DISCUSSION

To check the functioning of the spectrocoulometric cell, we used the system $\text{Fe}(\text{bipy})_3^{3+}/\text{Fe}(\text{bipy})_3^{2+}$ in acidic buffered solutions. It is known⁴ that the complex $\text{Fe}(\text{bipy})_3^{3+}$ formed by electro-oxidation of $\text{Fe}(\text{bipy})_3^{2+}$ undergoes a follow-up

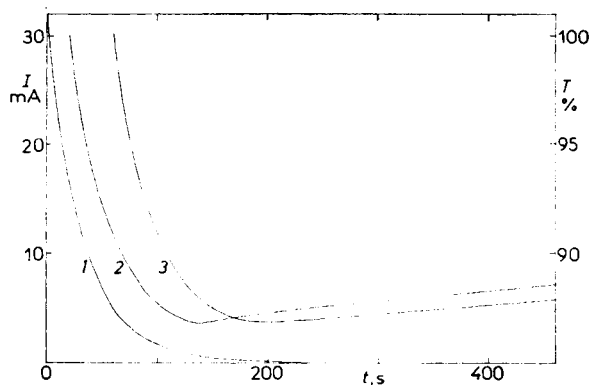


FIG. 3

Course of a spectrocoulometric experiment. 1 Current I as function of time, 2 time dependence of transmittance T with interruption of electrolysis at the minimum of T , 3 T - t dependence without interruption of electrolysis. $1 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ Fe}(\text{bipy})_3^{2+}$, $\text{pH} = 4.30$, equilibrium concentrations $[\text{Ac}^-] = 3.93 \cdot 10^{-2} \text{ mol dm}^{-3}$, $[\text{bipy}] = 6.2 \cdot 10^{-3} \text{ mol dm}^{-3}$; $E = 1.000 \text{ V vs SCE}$, $\lambda = 650 \text{ nm}$

chemical reaction, *i.e.* hydrolysis with the formation of an oxo-bridged complex, $(\text{bipy})_2\text{Fe}(\text{H}_2\text{O})\text{—O—Fe}(\text{H}_2\text{O})(\text{bipy})_2^{4+}$, where the oxidation state of Fe(III) remains unchanged. The follow-up reaction cannot be followed coulometrically, since its product is electroinactive at the potential of oxidation of $\text{Fe}(\text{bipy})_3^{2+}$, having no influence on the current-time curve. However, our spectrocoulometric system permits to follow the concentration-time dependence for $\text{Fe}(\text{bipy})_3^{3+}$ by measuring the optical transmittance or absorbance. The measurements were carried out at a wavelength $\lambda = 650 \text{ nm}$ corresponding to the absorption band of $\text{Fe}(\text{bipy})_3^{3+}$.

Comparison of Spectrocoulometry with Chronopotentiometry

Hydrolysis of the complex $\text{Fe}(\text{bipy})_3^{3+}$ is base-catalysed⁴ and the reaction rate is given by the kinetic equation

$$-\frac{dc}{dt} = c \sum_i k_i [B_i], \quad (1)$$

where c denotes concentration of $\text{Fe}(\text{bipy})_3^{3+}$ at time t , k_i is the rate constant of the second order corresponding to the i -th base, whose concentration is $[B_i]$. The values of the partial rate constants k_{OH^-} , $k_{\text{H}_2\text{O}}$ and k_{bipy} in solutions containing no buffer except for bipy and bipy H^+ at ionic strength 2.0 mol dm^{-3} were determined chronopotentiometrically⁴. For the sake of comparison, analogous measurements were carried out under the same conditions in the present work by the spectrocoulometric method with open-circuit relaxation. The circuit was opened after attainment of the minimum of transmittance T (Fig. 3); afterwards only hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$ took place. The T - t dependence was transformed into $\ln A$ - t (Fig. 4); the linearity of the transformed dependence suggests that the reaction is of the first order. Its

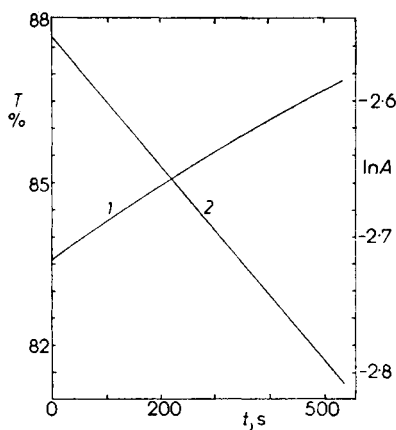


FIG. 4

Course of a spectrocoulometric open-circuit experiment. 1 T - t dependence, 2 $\ln A$ - t dependence. Initial concentration of $\text{Fe}(\text{bipy})_3^{3+} = 1.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 4.3$; $[\text{Ac}^-] = 3.93 \cdot 10^{-2} \text{ mol dm}^{-3}$, $[\text{bipy}] = 6.2 \cdot 10^{-3} \text{ mol dm}^{-3}$

slope gives the overall rate constant k :

$$k = k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{bipy}}[\text{bipy}]. \quad (2)$$

To find the values of the partial rate constants k_i , the composition of the solutions was varied in order to obtain from the measurements more equations than the number of unknowns, *i.e.* more than 3. We used five solutions differing in their composition. The obtained results were treated by multiple linear regression to obtain the k_i values. The experiments were planned in order to permit a very simple, although not too accurate checking of the calculated results. The solutions were therefore prepared so that pairs of solutions could always be found differing only by the concentration of one base. It was then possible to find the contribution of a given base, k_{Bi} , to the overall rate constant k from the dependence $k = f([B_i])$.

Comparison of the results with those of ref.⁴ was done in two ways:

1. Values of k_{Bi} were compared directly (Table I).
2. The overall rate constant k was calculated from Eq. (2) for a given solution composition from both the values of k_{Bi} in ref.⁴ and those obtained by multiple linear regression. This led to values of k_1 and k_2 (Table II). For comparison the "unsmoothed" values of k_3 calculated from the $\ln A-t$ dependence are also given.

The results given in Tables I and II show a principal agreement between the spectrocoulometric results and those of ref.⁴ concerning mainly the overall rate constant k . Some disagreement exists between the values of k_{bipy} , however, the contribution of this quantity to the value of k is relatively small, and if the concentrations of non-protonated 2,2'-dipyridyl in the solutions used do not differ very much, then the value of k_{bipy} calculated by regression is comparable with experimental errors, hence not reliable. The standard deviation of the value of k_{bipy} cannot be found from ref.⁴, but we assume that the result obtained by spectrocoulometry with objective evaluation by computer is more reliable.

TABLE I

Partial rate constants $k_{\text{H}_2\text{O}}$ (s^{-1}), k_{bipy} and k_{OH^-} ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$) for hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$ obtained by different methods at 25°C; $I = 2.0 \text{ mol dm}^{-3}$

k_{Bi}	From ref. ⁴	Graphically from 2 points	From multiple lin. regression	Standard deviation
$k_{\text{H}_2\text{O}}$	$8.4 \cdot 10^{-4}$	—	$6.72 \cdot 10^{-4}$	$3.12 \cdot 10^{-5}$
k_{bipy}	$4.1 \cdot 10^{-3}$	$4.27 \cdot 10^{-2}$	$4.09 \cdot 10^{-2}$	$7.95 \cdot 10^{-3}$
k_{OH^-}	$4.3 \cdot 10^5$	$3.17 \cdot 10^5$	$2.32 \cdot 10^5$	$2.59 \cdot 10^4$

Influence of Acetate Ions on Hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$

To study the influence of other bases (*e.g.* buffer components) on the hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$, we repeated the measurements in acetate buffer solutions. In this case

TABLE II

Overall rate constants for hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$ at 25°C. $I = 2.0 \text{ mol dm}^{-3}$; c_{bipy} and σ_{bipy} denote analytical concentration and dissociation degree of 2,2'-bipyridyl calculated as $\sigma = K_{\text{bipy}}/([\text{H}^+] + K_{\text{bipy}})$, where the dissociation constant $K_{\text{bipy}} = 10^{-4.54}$ (ref.¹¹); $[\text{bipy}]$ denotes equilibrium concentration of non-protonated 2,2'-bipyridyl. Rate constant k_1 was calculated from the values of k_{B1} given in ref.⁴, k_2 from those obtained by multiple linear regression, and k_3 from the experimental $\ln A-t$ curve; Eq. (2) was used for k_1 and k_2 . Total concentration of Fe^{2+} ions $c_{\text{Fe}^{2+}} = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{bipy}] = (c_{\text{bipy}} - 3c_{\text{Fe}^{2+}}) \sigma_{\text{bipy}}$

pH	$[\text{OH}^-] \cdot 10^{-10}$, mol dm^{-3}	c_{bipy} mol dm^{-3}	σ_{bipy}	$[\text{bipy}] \cdot 10^3$ mol dm^{-3}	$k_1 \cdot 10^4$, s^{-1}	$k_2 \cdot 10^4$, s^{-1}	$k_3 \cdot 10^4$, s^{-1}
3.50	0.316	0.100	0.0836	8.11	8.9	9.2	7.4
3.95	0.891	0.059	0.204	11.4	9.3	11.6	11.5
4.70	5.01	0.0100	0.591	4.14	10.7	9.6	10.2
5.50	31.6	0.0120	0.901	8.11	22.3	17.4	17.3
3.95	0.891	0.0050	0.204	0.41	8.8	7.1	6.8

TABLE III

Composition of $\text{Fe}(\text{bipy})_3^{2+}$ solutions under study. $t = 25^\circ\text{C}$, $I = 0.5 \text{ mol dm}^{-3}$, $[\text{Ac}^-]$ denotes equilibrium concentration of non-protonated acetate anions, other symbols as in Table II; $c_{\text{Fe}^{2+}} = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{bipy}] = (c_{\text{bipy}} - 3c_{\text{Fe}^{2+}}) \sigma_{\text{bipy}}$

pH	$[\text{OH}^-] \cdot 10^{10}$, mol dm^{-3}	$c_{\text{bipy}} \cdot 10^2$, mol dm^{-3}	σ_{bipy}	$[\text{bipy}] \cdot 10^3$, mol dm^{-3}	$c_{\text{Ac}^-} \cdot 10^2$, mol dm^{-3}	σ_{Ac^-}	$[\text{Ac}^-] \cdot 10^2$, mol dm^{-3}
3.50	0.316	10.0	0.0836	8.10	50.0	0.0532	2.66
3.90	0.794	6.00	0.186	10.6	50.0	0.123	6.15
4.30	2.00	2.00	0.365	6.20	15.0	0.262	3.93
4.70	5.01	1.00	0.591	4.14	5.00	0.471	2.35
5.10	12.6	1.00	0.784	5.49	2.50	0.691	1.73
5.50	31.6	0.500	0.901	1.80	2.50	0.849	2.12
3.90	0.794	0.500	0.186	0.37	50.0	0.123	6.15
4.70	5.01	1.00	0.591	4.14	50.0	0.471	23.5
5.50	31.6	0.988	0.901	6.20	4.63	0.849	3.93

Eq. (2) is rewritten in the form

$$k = k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{bipy}}[\text{bipy}] + k_{\text{Ac}^-}[\text{Ac}^-]. \quad (3)$$

Open-circuit spectrocoulometric measurements were carried out with nine solutions, whose variable composition permitted calculation of all the partial rate constants k_{Bi} as well as the approximate graphical determination of k . The composition of the solutions is given in Table III and the results are given in Tables IV and V. Comparison of the results in Tables I and IV suggests that the values of k_{Bi} obtained at

TABLE IV

Partial rate constants for hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$ at 25°C, $I = 0.5 \text{ mol dm}^{-3}$ ($k_{\text{H}_2\text{O}}$ in s^{-1} units, others in $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$); s standard deviation of the value obtained by regression (same dimension). For the calculation of the reliability interval $n = 9$, and $t_{5,0.05} = 2.571$

k_{Bi}	Graphically from 2 points	By multiple lin. regression	s	$st_{v,\alpha}/\sqrt{n}$
$k_{\text{H}_2\text{O}}$	—	$1.23 \cdot 10^{-5}$	$7.65 \cdot 10^{-5}$	$6.6 \cdot 10^{-5}$
k_{OH^-}	$2.4 \cdot 10^5$	$4.96 \cdot 10^5$	$0.67 \cdot 10^5$	$0.57 \cdot 10^5$
k_{bipy}	$1.0 \cdot 10^{-1}$	$1.32 \cdot 10^{-1}$	$0.27 \cdot 10^{-1}$	$0.23 \cdot 10^{-1}$
k_{Ac^-}	$4.5 \cdot 10^{-2}$	$5.80 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$1.03 \cdot 10^{-2}$

TABLE V

Overall rate constants for hydrolysis of $\text{Fe}(\text{bipy})_3^{3+}$ in acetate buffer solutions at 25°C, $I = 0.5 \text{ mol dm}^{-3}$; k_1 from Eq. (3) using k_{Bi} obtained by multiple linear regression, k_2 from the experimental $\ln A-t$ dependence

	$k_1 \cdot 10^3,$ s^{-1}	$k_2 \cdot 10^3,$ s^{-1}
	2.60	2.75
	4.99	4.70
	3.18	3.20
	2.13	2.20
	2.33	2.40
	3.01	2.73
	3.64	3.64
	14.47	14.50
	4.65	4.89

different conditions are significant except for the value of $k_{\text{H}_2\text{O}}$ in acetate buffer solutions. Owing to a high contribution of k_{Ac} to the overall rate constant k the contribution of $k_{\text{H}_2\text{O}}$ (which is small even in absence of acetates) is difficult to distinguish from experimental errors.

The results in Table V show a very good agreement between the values of k obtained from the $\ln A-t$ dependences after interruption of electrolysis and those calculated from Eq. (3) with the use of the values of k_{Bi} obtained by multiple linear regression. It is thus seen that the scatter of the results of measurements is acceptably low.

The obtained results show that the newly developed spectrocoulometrical measuring apparatus¹² is suitable for studies of chemical reactions coupled with the electrode process and yields new possibilities in spectroelectrochemical studies of the kinetics and mechanism of chemical reactions. In contrast to coulometry, the new technique can be used for identification of intermediates or final products of chemical reactions coupled with the electrode process. This was shown in another case by recording the whole absorption spectrum of a solution in the spectrocoulometric cell with the rapid scanning spectrophotometer⁸. In our paper⁸ there were indicated instrumental variants of the spectrocoulometric technique, however, only qualitative observations were performed; quantitative data are firstly presented just in this work. From the standpoint of nomenclature it should be stressed that our spectrocoulometric method is considerably different from spectrocoulometry mentioned earlier¹³, in which a working electrode of small dimensions was placed in a thin-layer cell and the mass transport to and from the electrode was controlled by diffusion. We use the term spectrocoulometry to indicate that the experimental conditions are the same as in classical potentiostatic coulometry, including stirring and the use of a macro-electrode.

REFERENCES

1. Kuwana T., Winograd N.: *Electroanalytical Chemistry* (A. J. Bard, Ed.) Vol. 7. Marcel Dekker, New York 1974.
2. Heineman W. R.: *Anal. Chem.* 50, 390 A (1978).
3. Lapkowski M., Strojek J. W.: *Roczn. Chem.*, in press.
4. Ehman D. L., Sawyer D. T.: *Inorg. Chem.* 8, 900 (1969).
5. Mocák J., Németh M.: *Highly Effective Coulometric Cell with Uniform Potential Distribution across the Working Electrode*. Czech. PV 5299—85.
6. Németh M., Mocák J.: *This Journal* 51, 636 (1986).
7. Strojek J. W., Kuwana T.: *J. Electroanal. Chem. Interfacial Electrochem.* 16, 471 (1968).
8. Lapkowski M., Strojek J. W., Németh M., Mocák J.: *Anal. Chim. Acta* 171, 77 (1985).
9. Bard A. J., Santhanam K. S. V.: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 4. Marcel Dekker, New York 1971.
10. Meites L.: *Physical Methods of Chemistry, Part II A, Electrochemical Methods* (A. Weissberger and B. W. Rossiter, Eds). Wiley, New York 1971.

11. Martell A. E., Smith R. M.: *Critical Stability Constants*, Vol. 5, p. 248. Plenum Press, New York 1971.
12. Mocák J., Németh M.: *Spectrocoulometric Macrocell with Direct View Optical Probe and the Way of its Use*. Czech. PV 5296—85.
13. Kuwana T., Heineman W. R.: *Acc. Chem. Res.* 9, 241 (1976).

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