Electrochemical resolution of CN-linkage isomers in the course of the reaction of $[Cr(CN)_2(H_2O)_3NO]$ with Hg^{2+} ions

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Transformation by semi-differentiation was employed to raise resolving power of voltammetry with a stationary hanging mercury drop electrode. This technique was applied to analyze components with small difference in half--wave potentials using the method of subtraction of the peak of one component from the curve of coinciding peaks for the analysis of intermediates and products of multistep reaction of $[Cr(CN)_2(H_2O)_3NO]$ with Hg^{2+}

Разработано преобразование посредством семи-дифференцирования для повышения разрешающей способности вольтамметрии с неподвижно висящим ртутным капельным электродом. Это усовершенствование было применено для анализа компонентов с малым различием в величинах потенциалов полуволн методом вычитания пика одного компонента из кривой налагающихся пиков для анализа интермедиатов и конечных продуктов многостадийной реакции $[Cr(CN)_2(H_2O)_3NO]$ с Hg^{2+}

In our previous papers [1—4] we reported the results of our study of chromium-linkage isomers formed in the course of the reaction of $[Cr(CN)(H_2O)_4NO]^+$ with Hg^{2+} and Ag^+ ions. Experimental techniques used comprised polarography, linear scan voltammetry (LSV), and spectrophotometry in the visible spectral region. Absorption *vs.* time dependence measurement and following the limiting diffusion currents of complexes formed in the course of reaction made it possible to determine its rate and equilibrium parameters.

These experimental techniques have also been applied in our study of the $[Cr(CN)_2(H_2O)_3NO]$ reaction with Hg^{2+} ions [5]. This reaction is more complicated because of the great number of multinuclear complexes with CN bridges that may arise from it. Table 1 gives the possible multinuclear complexes formed in the course of the reaction (*VI*, *VIII*, *X*, *XI*) as well as the corresponding Cr complexes formed by the electrode reduction of Hg(II) (*VII*, *IX*, *III*). Comparison of the data given in Table 1 reveals that the spectral properties of pairs of complexes *I*—*II*, *III*—*IV*, *V*—*VI*, *IX*—*X* are not sufficiently different for the purpose of determining the concentration of single complexes in the reaction mixture.

Table 1

Comparison of spectrophotometric and voltammetric properties of complexes [1—7]
pH = 2.1, ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}), T = 276 K

No.	Species	Spectrophotometry λ_{max}/nm (ε_{max}/(mol^{-1} dm^3 cm^{-1}))	Polarography $E_{1/2}$ vs. SCE/V	Number of exchanged electrons on Cr
I	$NO(H_2O)_4Cr—CN^+$	370 (211) 450 (120) 610 (37)	−1.21	3
II	$NO(H_2O)_4Cr—CN—Hg^{3+}$	372 (264) 445 (144) 610 (48)	(+0.3) −1.21	2 3
III	$NO(H_2O)_4Cr—NC^+$	385 (153) 445 (158) 610 (31)	−0.98	3
IV	$NO(H_2O)_4Cr—NC—Hg^{3+}$	392 (157) 445 (163) 603 (32.5)	+0.005 −0.98	2 3
V	$NO(H_2O)_3Cr(CN)_2$	365 (296) 454 (108) 630 (24)	−1.12	3
VI	$NO(H_2O)_3Cr(CN—Hg—NC)_2Cr(H_2O)_3NO^{4+}$	368 (334)* 450 (120) 422 (34)	(+0.3) −1.12	2 3
VII	$NO(H_2O)_3Cr(NC)(CN)$		−0.905	3
VIII	$NO(H_2O)_3Cr(NC—Hg—NC)(CN—Hg—CN)Cr(H_2O)_3NO^{4+}$		−0.02 −0.905	2 3
IX	$NO(H_2O)_3Cr(NC)_2$	389 (97)* 445 (102) 612 (20)	−0.66	3
X	$NO(H_2O)_3Cr(NC—Hg—CN)_2Cr(H_2O)_3NO^{4+}$	388 (101) 442 (105) 608 (22)	−0.02 −0.66	2 3
XI	$NO(H_2O)_4Cr—NC—Hg—CN^{2+}$		*ca.* 0.0 −0.98	2 3

* Preliminary data.

The present paper deals with the electrochemical resolution of complexes using high scan rate deconvolution voltammetry.

Experimental

All the chemicals used were of anal. grade without any further refining. Compound $K_3[Cr(CN)_5NO]\cdot H_2O$, parent species for preparing the $[Cr(CN)_2(H_2O)_3NO]$ complex was prepared according to the procedure described in [8, 9]. $[Cr(CN)_2(H_2O)_3NO]$ was produced [6] by acid hydrolysis of $[Cr(CN)_5NO]^{3-}$ in solution, with pH adjusted continuously during the preparation process to a value higher or equal to 3. The solution was then purified of cation complexes by being poured through a short column of cation exchange resin DOWEX 50 W X-8 in an Na^+ cycle and its exact concentration was established spectrophotometrically after oxidation by H_2O_2 to chromate in an alkaline medium.

Electrochemical measurements were made with a GWP 673 (AW DDR) polarograph on line with a microcomputer (Compucorp, USA) equipped with AD, DA converters (Burr—Brown). The computer allows a minimum sampling time of 0.2 ms. Experimental curves recorded into the computer (as a rule 1000 values sampled in each experiment) were semi-differentiated using a fast computer program based on the Grünwald definition [10] of the n-th order differintegration, d^n/dt^n The program enabled a simultaneous graphical presentation of the computed function on an XY recorder (VEB Messapparatewerk Schlotheim), the computing rate, *ca.* 2 values per second, was suitable for mechanical recording.

The transformed (semi-differentiated) curve was stored into the peripheral memory for further processing. The LSV curve of the component for the correction was scanned and transformed in a similar way. The accuracy of the correction by subtraction was controlled visually [11].

Results and discussion

Using polarographic analysis it was possible to resolve the mentioned pairs of complexes, *I—II*, *III—IV*, *V—VI*, *IX—X*, *III—XI*, to such a degree that Hg(II) complexes exhibited a more positive two-electron reduction wave in addition to a three-electron reduction wave common to both species of the above-mentioned pairs. Unfortunately, Hg(II) reduction potentials of individual multinuclear Hg complexes as well as of the Hg—aquacomplex do not differ sufficiently for their resolution in the case of an excess of the Hg—aquacomplex which is necessary for the existence of some of them. From Table 1 it also follows that in the case of pairs *III—VII*, *IV—VIII*, *VIII—XI* polarography is inadequate to resolve even the negative waves (in the − 0.9 V *vs.* SCE region). Moreover, the polarographic experiment is often too slow to provide enough current-potential curves in the course of the relatively fast reaction of $[Cr(CN)_2(H_2O)_3NO]$ with Hg^{2+}

The difficulty caused by the slowness of the method may be overcome by using LSV [12]. The resolving power of this method is rather low due to the lack of symmetry of the current response peaks. It may, however, be considerably increased by properly transforming experimentally obtained current-potential curves. The semi-differentiation of current-potential (time) dependences may serve as a suitable transformation technique [13]. In LSV ($E = E_{\text{initial}} + kt$), semi-differentiation $d^{1/2} I/dt^{1/2}$ is proportional to $d^{1/2} I/dE^{1/2}$. The dependence of this quantity on E exhibits a symmetrical maximum with the maximum potential [13, 14] equal to the reversible or irreversible reduction half-wave potential. For irreversible electrode processes (reductions corresponding to peaks resolved in this paper are irreversible) the width of the peak, at half its height, equals $2.94R\ T/$ $/(\alpha \cdot z_a \cdot F)$, where z_a is the number of exchanged electrons in the slowest electrode reaction stage and α is the charge transfer coefficient. The height of the peak is directly proportional to concentration c with a direct proportionality coefficient equal to $\alpha \cdot z_a \cdot z\ F^2 \cdot A \cdot v \cdot \sqrt{D}/(3.367R\ T)$, where A is the surface area of the electrode, v — the scan rate, z — the number of exchanged electrons in the overall electrode reaction, and D is the diffusion coefficient of the analyzed species [13, 14]. Examples of such a transformation can be seen, for a system with three electroactive components, in Fig. 1 and for that with four such components in Fig. 2, where curves *1* are voltammetric and curves *2* are the transformed curves.

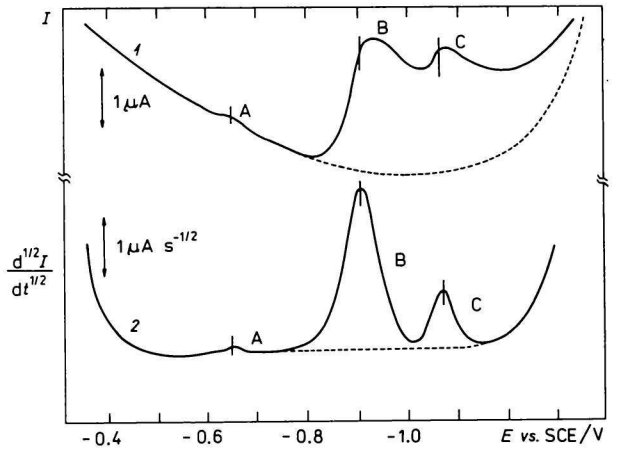


Fig. 1. Linear scan voltammogram (*1*) and semi-differentiated voltammogram (*2*): $c([Cr(CN)_2(H_2O)_3NO]) = 0.25$ mmol dm^{-3}; $c(Hg^{2+}) = 2.5$ mmol dm^{-3}; time after mixing 70 s; $T = 276$ K; pH = 2.1; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}); scan rate 1 V s^{-1}; hanging mercury drop electrode (HMDE), surface area 1.64 mm^2; negative reduction peaks A — of complex *X* (Table 1), B — of complex *VIII*, and C — of complex *VI*; dash line — $c(Hg^{2+}) = 2.5$ mmol dm^{-3}

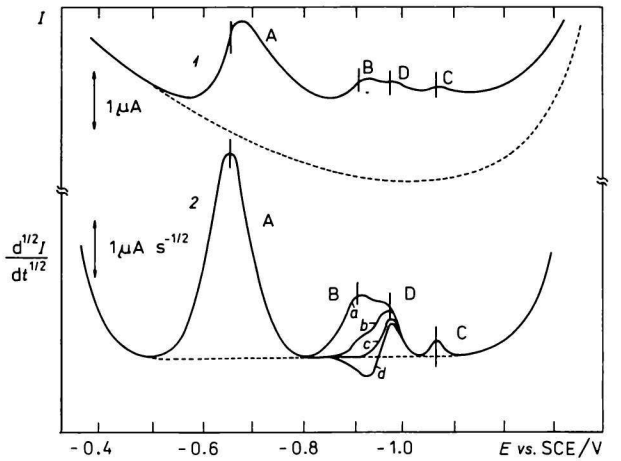


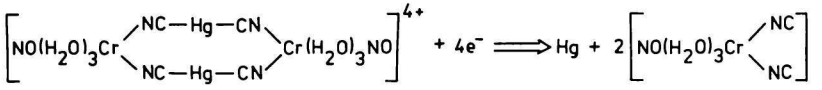
Fig. 2. Linear scan voltammogram (*1*) and semi-differentiated voltammogram (*2*): $c([Cr(CN)_2(H_2O)_3NO]) = 0.25$ mmol dm^{-3}; $c(Hg^{2+}) = 2.5$ mmol dm^{-3}; time after mixing 350 s; $T = 276$ K; pH = 2.1; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}); scan rate 1 V s^{-1}; hanging mercury drop electrode (HMDE) of 1.64 mm^2. Negative reduction peaks A — of complex *X* (Table 1), B — of complex *VIII*, D — of complex *XI*, and C — of complex *VI*. Graphic representation of the computer technique for current subtraction of one component in analyzing the peak of two overlapping components: *a*) original curve; *b*) insufficient subtraction; *c*) correct subtraction; *d*) excessive subtraction of complex *XI* current (Table 1); dash line — $c(Hg^{2+}) = 2.5$ mmol dm^{-3}

The reaction of $[Cr(CN)_2(H_2O)_3NO]$ complex with Hg^{2+} proceeds according to the scheme proposed on the basis of analogous reaction of $[Cr(CN)(H_2O)_4NO]^+$ with Hg^{2+} described in paper [4]

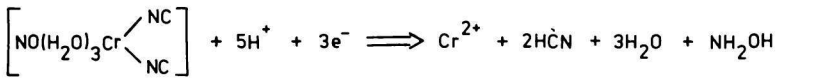
$$V + Hg^{2+} \rightleftharpoons VI \rightarrow VIII \rightarrow X \rightarrow XI \qquad (A)$$

(Numbers of complexes in the scheme agree with those in Table 1.)

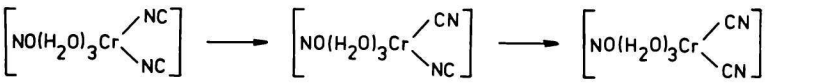
Individual complexes have been analyzed on the basis of their negative reduction peaks growing on the Hg(II) reduction current background. Electrode reaction equations for complex *X* selected for illustration, are as follows



(B)



(C)



(D)

Reaction (D) is competitive and parallel with reaction (C), which fact should be taken account of in evaluating voltammograms.

Curves *2* and *2a* in Figs. 1 and 2, respectively, are illustrations of transformed voltammograms recorded in the course of the reactions.

Fig. 1 shows three peaks: A is that of complex *IX* reduction (Table 1), B — of complex *VII* and C — of complex *V* reductions, respectively.

Such an interpretation followed from comparison with the analogous reaction of $[Cr(CN)_2(H_2O)_4]^+$ [12] as well as from our study of $[Cr(CN)(H_2O)_4NO]^+$ [1—4]. Just as in the cited studies, so for $[Cr(CN)_2(H_2O)_3NO]$ reactions (A) and (D) a mechanism has been proposed in which the decomposition of the original σ bond and the formation of a new one proceed without CN dissociation through an intermediate with the

$$\mathrm{Cr}\ldots\begin{array}{c}\mathrm{C{-}Hg}\\ \|\\ \mathrm{N}\end{array} \quad \text{or } \mathrm{Cr}\ldots\begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{N}\end{array}\ \pi \text{ bond.}$$

Fig. 1 represents a deconvolution voltammogram, characteristic of initial reaction phases. The sum of the peak heights is virtually constant for a period of 100 s from the start of the reaction. In computing the concentrations of individual components it has been assumed that the coefficient of proportionality between them and the signal is in all cases the same (equal D, z_a, z, α).

In later reaction phases (100—600 s) there is a drop in the sum of the currents of A, B, and C peaks and at the same time a decrease of the symmetry of peak B in the direction of negative potentials. Towards the end of this phase, the peak became sharp again but the maximum potential had shifted, with respect to the original peak B, by 75 mV towards the negative values. This peak grew as the reaction proceeded. It is likely that this peak is connected with the complex *XI* reduction.

In the reaction time of 100 to 600 s there appeared, on the deconvolution voltammogram, unresolved peaks with $\Delta E_{max} \doteq 75$ mV, so that they could not be directly analyzed.

For their resolution a simple method was used, similar to that employed by *Bond* and *Grabaric* [11] for resolving peaks of the differential pulse polarography. The said authors worked with stable components of the analyzed system and from the record of an unresolved double-peak they subtracted, by means of a computer, the peak of one pure component registered for various concentrations. In our case we had to start from the record in Fig. 1, made when the concentration of complex *XI* was negligible. Curves belonging to a varied complex *VIII* concentration (Table 1) were computed on the basis of the assumed signal linear dependence on concentration. Successive subtractions of these curves from the unresolved record were also made with the aid of a computer. Since, similarly as in the case of the differential pulse polarography, peaks are of a symmetrical shape in the deconvolu-

tion LSV as well, it was possible to check the correct height of the subtracted peak visually, as was done by the authors of paper [11]. Fig. 2 is an example of such a procedure. Curve *a* illustrates the original unresolved peak, curve *b* shows the state when a peak of a rather low concentration of complex *VIII* has been subtracted, *c* is the curve recorded after the subtraction of the right concentration, and *d* the curve drawn after the subtraction of the peak belonging to a higher concentration of complex *VIII* than that of the reacting solution.

On the basis of the currents of peaks of individual components thus obtained at different reaction times we could get time profiles of the separate components present in the reaction mixture. Relative concentration values of complexes $R = c_x/c_{o,V}$ (where x are numbers from Table 1) in the course of the reaction of $[Cr(CN)_2(H_2O)_3NO]$ with Hg^{2+} are given in Table 2. Time dependences of concentrations of individual complexes, given in Fig. 3, are a confirmation of the assumption that the reaction has proceeded as a consecutive reaction in three relatively slow steps (*A*). The formation of complex *VI* from *V* and Hg^{2+} (*A*) is a fast substitution reaction of the Hg(II) coordination sphere. Since the experiments have been made with a large excess of Hg^{2+}, it has been assumed that the equilibrium has markedly shifted in favour of *VI* [4].

Table 2

Time dependence of relative concentration of complexes $R_x = c_x/c_{o,V}$ (numbers according to Table 1) in the course of reaction of $[Cr(CN)_2(H_2O)_3NO]$ (initial concentration $c_{o,V} = 0.25$ mmol dm^{-3}) with Hg^{2+} (initial concentration 2.5 mmol dm^{-3}), pH = 2.1, $T = 276$ K, ic strength 1 mol dm^{-3} (ClO_4^-, Na^+ H^+, Hg^{2+})

t/s	R_V	R_{VIII}	R_X	R_{XI}	Σ
0	1.00	—	—	—	1.00
30	0.74	0.28	0.05	—	0.97
70	0.31	0.49	0.18	—	0.98
120	0.15	0.46*	0.33	0.02*	0.96
200	0.05	0.28*	0.60	0.03*	0.96
300	0.025	0.14*	0.76	0.04*	0.965
400	0.015	0.07*	0.83	0.045*	0.96
500	0.005	0.03*	0.87	0.05*	0.955
600	—	0.01*	0.89	0.055*	0.955
1000	—	—	0.90	0.08	0.98
5000	—	—	0.76	0.20	0.96
10000	—	—	0.74	0.23	0.97
20000	—	—	0.63	0.33	0.96
30000	—	—	0.55	0.40	0.95

* Values obtained by the resolution of overlapping peaks.

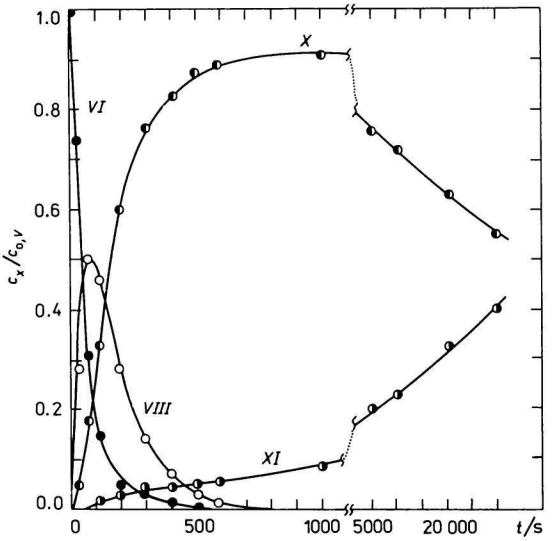


Fig. 3. Concentration time profiles of Hg complexes in the course of reaction (*A*): $c([Cr(CN)_2(H_2O)_3NO]) = 0.25$ mmol dm^{-3}; $c(Hg^{2+}) = 2.5$ mmol dm^{-3}; pH = 2.1; $T = 276$ K; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}).

In registering experimental voltammetric dependences it is unavoidable to use high scan rates because reduction primary products, according to (*B*), are subject to spontaneous monomolecular reactions in which more stable linkage isomers of chromium cyanide complexes are formed (*D*) [15]. To get correct results it is necessary to let minimum time elapse between the generation (at *ca.* 0 V *vs.* SCE) and the detection of voltammetrically resolved chromium cyanide complexes. That is why the highest possible scan rate should be used. Since the charging currents rise proportionally with the increasing scan rate, it is considered that the optimal scan rate is 1 V s^{-1}.

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