

ANALYSIS OF THE ELECTRODE KINETICS OF Ni(II) REDUCTION IN THIOCYANATE MEDIA ON THE DROPPING MERCURY ELECTRODE

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A study of two prewaves of the Ni(II)-SCN⁻ system was carried out under the experimental conditions when the influence of electroreduction of SCN⁻ is negligible. Kinetics of Ni(II) reduction in thiocyanate media on the dropping mercury electrode was studied by DC Tast Polarography (DC_TP) via determination of Koutecký's parameter χ ; the influence of different variables was analyzed. The study of prewaves was performed using various polarographic techniques. Values of χ depend on the SCN⁻ concentration, pH, ionic strength (Ψ -effect) and on the nature of the supporting electrolyte. The number of electrons n , the transfer coefficient α , the stoichiometric number ν , ΔH^\ddagger , and ΔS^\ddagger were determined (compensation effect). The first prewave has character of a reaction in the solution, the second prewave is a surface process. Main features of both mechanisms are common: catalytic nature, one-electron step discharge and the rate-determining process between species of opposite charges.

Key words: Catalytic prewaves; Polarography; Kinetics; Nickel(II) thiocyanate; Electroreduction; Electrochemistry.

Electrocatalysis of the metal ion reduction on mercury by adsorbed ligands has been the subject of a recent review¹ from which two features are apparent: first, polarography has been the most informative method, especially from theoretical aspects and, second, a number of systems show catalytic prewaves.

Different papers appeared in the literature on the electrode reactions of nickel(II)-thiocyanate, but only a schematic view of the mechanism was given and, besides, there is disagreement among proposed mechanisms²⁻⁴. These reactions are quite complex because the electroreduction of thiocyanates^{5,6} is parallel to formation of NiS on the electrode surface. Studies of these side reactions revealed that the adsorbed NiS may influence the kinetics of the reaction responsible for the appearance of the prewaves^{7,8}.

When Ni(II) ions are discharged on a dropping mercury electrode (DME) in aqueous solution, thiocyanate displays two polarographic prewaves⁹. We

have shown¹⁰ that both prewaves exhibit a catalytic character, although the second prewave is also slightly limited by an adsorption. Details on the formation of electrochemically active compounds, responsible for the appearance of both prewaves, are far from being clear and the electrochemical behaviour of Ni²⁺ species on the DME in presence of SCN⁻ is still an open question and its kinetics should be explored.

The system is one of the model systems which we have been studied by fast polarography¹¹. From our experience with Ni²⁺-pyridine (ref.¹¹) and other systems^{12,13}, we suggest that Koutecký's parameter χ can be used as an experimental rate constant, implying that we employ a relaxation method. The study of the χ -function is a good way to understanding the mechanism of this type of reactions. This paper is on kinetic and electrochemical study of the Ni(II)-SCN⁻ system to improve the formulation of its reaction mechanisms.

EXPERIMENTAL

All the chemicals (Merck) were of analytical grade. Solutions were prepared from water purified by passage through a Milli-Q system from Millipore.

The experimental conditions were optimized to resolve the two catalytic prewaves and to minimize the influence of NiS adsorption. Hence, the prewaves of Ni²⁺ ($1.0 \cdot 10^{-4}$ – $6.0 \cdot 10^{-4}$ mol dm⁻³) were investigated in the presence of an excess of KSCN ($4.0 \cdot 10^{-3}$ – $4.5 \cdot 10^{-2}$ mol dm⁻³). Solutions of electrolytes KNO₃ and alternatively LiNO₃, NaNO₃ or CsNO₃ (0.05–0.4 mol dm⁻³) provided constant ionic strength, *I*. To avoid hydrolysis of Ni²⁺, pH of solutions was kept between 3.0 and 8.0. The initial acidity was adjusted by adding to solutions of both reactants (Ni²⁺ and SCN⁻) few drops of very dilute solutions of HNO₃ or KOH and pH values were constant during all the experiments. Oxygen was removed from solutions with a stream of purified nitrogen passing for 15 min (and for another 1 min before each new experiment). The polarographic cell was thermostatted at 20–35 (± 0.1) °C. The electrode process was studied by direct current fast (DC_TP), normal pulse (NPP) and differential pulse polarography (DPP). All techniques were implemented with a Tacussel microprocessor unit connected to an automatic polarographic stand equipped with a DME, a Pt wire auxiliary electrode and the saturated calomel electrode (SCE) as a reference electrode. The drop time *t* was maintained mechanically at 3.0 s except in DC_TP when it was changed from 0.3 to 3.0 s. The scan rate was 5 mV s⁻¹, the potential range between -0.3 and -1.6 V and the DPP pulse amplitude 60 mV. pH measurements were made with a Radiometer 51 pH-meter.

RESULTS AND DISCUSSION

Kinetic Analysis

Thiocyanate proved to be polarographically inactive in KNO₃ supporting electrolyte, up to 0.4 mol dm⁻³ at pH 3.0–8.0. Addition of Ni²⁺ to the elec-

trolyte caused appearance of two Ni^{2+} prewaves in DC_TP (Fig. 1). The half-wave potentials $E_{1/2}$ for the prewaves in Fig. 1 were -0.73 ± 0.02 and -0.92 ± 0.02 V, compared with -1.13 ± 0.02 V for the reduction wave of Ni^{2+} in the absence of thiocyanate. Our previous results¹⁰ support the catalytic character of both prewaves although the second prewave has a mixed adsorption-catalytic character. Besides, the comparison of their $E_{1/2}$ values with the main wave indicates that prewaves correspond to reaction of Ni^{2+} complexes. With the participation of SCN^- the reduction takes place at potentials lower than Ni^{2+} complexes present in absence of thiocyanate in the supporting electrolyte. This fact is consistent with the catalytic character of prewaves. The main Ni^{2+} wave is diffusion controlled.

Average currents were corrected for the residual current at given potentials. In the case of the second-prewave limiting current, a correction was introduced taking into account superposition of the Ni^{2+} discharge process. Because of the sensitivity of catalytic prewaves to experimental conditions, the measurement of the heights of both prewaves and the main wave was repeated several times, for a set of given conditions. The agreement between values obtained was, in general, satisfactory and an average value was taken.

Increasing the stoichiometric concentration of SCN^- in the solution raised both the limiting currents of the first and the second prewaves up to 90% of the limiting current of Ni^{2+} reduction in the absence of SCN^- . This behaviour was reported for metal ions, where the maximum limiting cur-

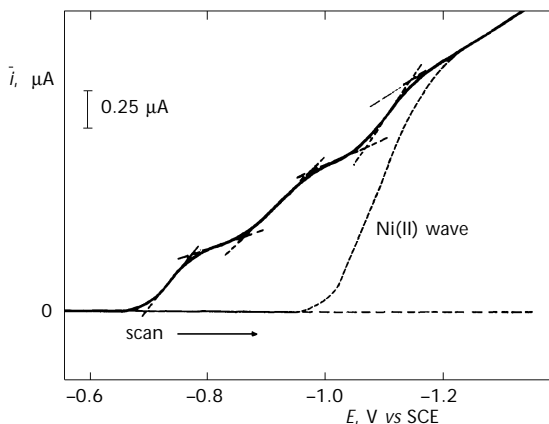


FIG. 1

DC_T polarograms for the system Ni(II)-SCN^- (—) and the Ni(II) species (----). $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

rent at high ligand catalyst concentration virtually coincides with the limiting diffusion current of the metal ion itself.

A similar behaviour has been observed by NPP and DPP for prewaves and prepeaks of Ni^{2+} in the presence of SCN^- . The peak current- SCN^- concentration dependence is similar to the Langmuir adsorption isotherm.

It seems reasonable to consider the appearance of a prewave as a special case of the irreversibility of the overall wave. According to results reported in refs^{12,13}, ratios \bar{i}_k/\bar{i}_d (\bar{i}_k limiting current of the first prewave, \bar{i}_d limiting current of the main wave) and $\Sigma\bar{i}_k/\bar{i}_d$ ($\Sigma\bar{i}_k$ limiting current of the second prewave) were taken as a function $F(\chi)$ of Koutecký's parameter^{14,15}. Hence the values of $F(\chi)$ were calculated from limiting currents while χ values were obtained by simulation as previously described¹³. The meaning of this parameter depends on the rate-determining step of the mechanism, but in all cases, χ has got a character of an experimental rate constant. The influence of different variables on this parameter has been analyzed in order to clarify the reaction mechanism responsible for the appearance of each prewave.

Accurate values of χ obtained for different concentrations of SCN^- (Fig. 2) confirmed our previous findings¹⁰ concerning the nature and the mecha-

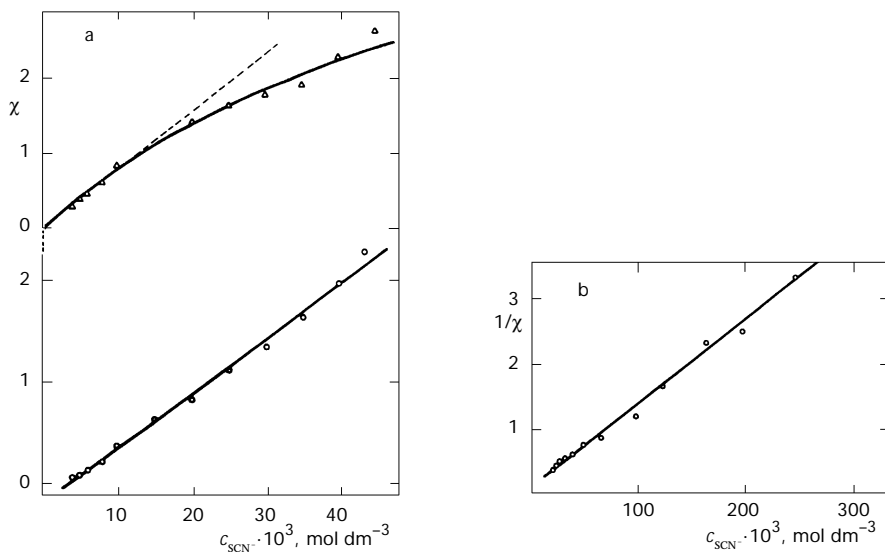


FIG. 2

The dependence of χ on the SCN^- concentration for the first prewave (O) and the second prewave (Δ). $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$ (a); plot of $1/\chi$ vs $1/c_{\text{SCN}^-}$ at the same conditions for the second prewave (b)

nism of the prewaves. The second prewave can be explained by a surface reaction while the first prewave represents a solution process. Hence, the whole reaction takes place partly in the adsorption layer at the electrode.

However, there is no unanimous view in the literature concerning the choice of an adsorption model for SCN^- species: Adsorption of SCN^- at a mercury electrode fits to Frumkin isotherm¹⁶ but at low surface coverage the Frumkin isotherm reduces to a Langmuir isotherm.

The sensitivity of the isotherm to experimental conditions, especially to the drop time t should be noted. Under our experimental conditions (Fig. 2), Langmuir model is valid for the species forming the second prewave. For comparative purposes, electrocapillary curves were obtained (Fig. 3) at the same experimental conditions as in Fig. 2. The first prewave is located in the vicinity of the point of zero charge (p.z.c.), where the SCN^- coverage of the electrode surface is higher than it corresponds to potential range of the second prewave. These findings confirm the origin of the first prewave in a solution process while the second prewave has a reliable surface nature.

On the other hand, the linear dependence of χ vs $t^{1/2}$ (Fig. 4) for both prewaves strongly suggests that adsorption on the DME surface very quickly attains equilibrium¹⁷. This fact supports the surface character assumed for the reactions of polarographically active compounds (PAC-I and PAC-II) which form prewaves in spite of their different origin.

The influence of Ni^{2+} on the peak current for the Ni^{2+} prepeaks in DPP was studied by DPP in 0.4 M KNO_3 and $8 \cdot 10^{-3}$ M SCN^- at pH 6.0. The peak

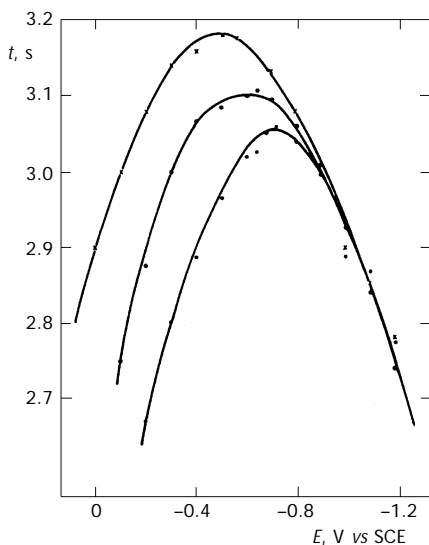


FIG. 3

Electrocapillary curves: $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3}$ (\times),
 $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3} + c_{\text{SCN}^-} = 8.0 \cdot 10^{-3}$ (\circ),
 $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3} + c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3} + c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$ (\bullet)

current is constant when Ni^{2+} concentration is changed from $1.0 \cdot 10^{-4}$ to $6.0 \cdot 10^{-4}$ mol dm^{-3} . Thus, an increase in the Ni^{2+} concentration does not decrease either the concentration of free ligand or its surface excess and no changes were observed for χ values.

Table I shows the dependence of Koutecký's parameter χ on the solvent acidity at $c_{\text{Ni}^{2+}} = 2.0 \cdot 10^{-4}$ mol dm^{-3} , $I(\text{KNO}_3) = 0.4$ mol dm^{-3} , $t = 1.5$ s, and $T = 298.15$ K. At higher pH, χ values for both prewaves were practically independent of pH while in acid solutions an increase of χ with decreasing pH was observed. This fact could be explained by superposition of catalytic hydrogen evolution analogous to other complexes of nickel and cobalt with sulfur-containing ligands^{18a}. Since the initial potential of the catalytic hydrogen evolution is close to the initial potential of the main wave (≈ -1.05 V vs SCE, $t = 1.5$ s), this process is not relevant in our case. The effect of pH is most likely due to an acid-catalyzed dehydration of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ preceding the mechanisms which explain the appearance of both prewaves^{12,13}.

The dependence of χ on the ionic strength I was also studied in the range from 0.05 to 0.4 mol dm^{-3} at $c_{\text{Ni}^{2+}} = 2.0 \cdot 10^{-4}$ mol dm^{-3} , $c_{\text{SCN}^-} = 2.0 \cdot 10^{-2}$ mol dm^{-3} , pH 6.0, $t = 1.5$ s, and $T = 298.15$ K (Table II). In ideal case the background electrolyte ions should not adsorb on the DME and their tendency to form complexes with Ni^{2+} should be low. Nitrates do not form complexes with Ni^{2+} (refs^{19,20}) but they adsorb on DME significantly²¹ being separated from the electrode surface by water molecules. A tentative fit of low χ vs

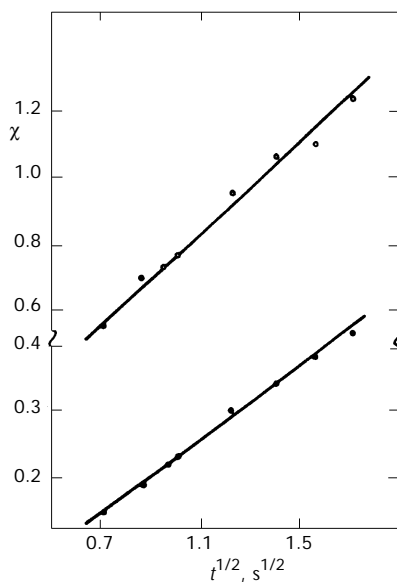


FIG. 4
Dependence of χ on the drop time for the first prewave (●) and the second prewave (○). $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4}$ mol dm^{-3} , $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3}$ mol dm^{-3} , $c_{\text{KNO}_3} = 0.4$ mol dm^{-3} , pH 6.0, $T = 298.15$ K

TABLE I
Dependence of χ on the solvent acidity^a

pH	$c_{\text{SCN}^-} \cdot 10^2, \text{ mol dm}^{-3}$					
	0.4		0.8		2.0	
	χ_{I}	χ_{II}	χ_{I}	χ_{II}	χ_{I}	χ_{II}
3.0	0.085	0.403	0.229	0.731		
3.5	0.081	0.378	0.227	0.700	0.907	1.439
4.0	0.076	0.350			0.871	1.370
4.5	0.068	0.3316	0.222	0.662	0.852	1.306
5.0	0.063	0.308	0.218	0.639	0.825	1.235
6.0	0.064	0.306	0.217	0.618	0.817	1.315
6.5	0.065	0.317			0.787	1.220
7.0	0.062	0.305	0.216	0.616		
7.5	0.065	0.306	0.216	0.609	0.778	1.230
8.0	0.065	0.298	0.216	0.620	0.808	1.254

^a Experimental conditions: see the text.

TABLE II
Dependence of χ on the ionic strength I^a

$I(\text{KNO}_3), \text{ mol dm}^{-3}$	First prewave	Second prewave
0.050	1.709	2.933
0.075	1.479	2.359
0.100	1.338	2.080
0.150	1.145	1.709
0.200	0.985	1.470
0.300	0.881	1.330
0.400	0.817	1.315

^a Experimental conditions: see the text.

$\sqrt{I} / (1 + \sqrt{I})$ was made by Guggenheim's correction²² of the Debye-Hückel theory. The first prewave was fitted by $\log \chi_I = 0.625 + 0.389 I - 2.25 I^{1/2}/(1 + I^{1/2})$ with $r = 0.9997$, and the second prewave was fitted by $\log \chi_{II} = 1.091 + 1.178 I - 3.73 I^{1/2}/(1 + I^{1/2})$ with $r = 0.9974$. These results strongly suggest the existence of kinetic salt effect in reactions responsible for both prewaves. So, in the case of the first prewave, a value very close to -2 was found for the z_+z_- product. However, for the second prewave a high value close to -4 was found in agreement with its surface character. These processes depend more strongly on ionic strength than the reactions in the solution. However, this number must be taken with care due to the limited validity of the Debye-Hückel-Guggenheim formula for interpreting surface processes. Anyway, the unambiguous negative values of these products show that processes responsible for both prewaves could be controlled by a reaction between two species of opposite charge. These findings are in agreement with the negative value of the charge of the activated complex z_{\pm} obtained by Kutner and Galus²³ for the reduction of Ni^{2+} in the presence of SCN^- from values of second virial coefficient.

A decrease in kinetic limiting currents (i_k and Σi_k) with rising ionic strength reflects the effect of the potential on the outer Helmholtz plane (Ψ , negative at potential of the prewave) on the rate of chemical reactions taking place at the electrode surface and involving cationic reactants. Figure 5 shows plots of $\ln \chi$ vs Ψ , where Ψ values were taken from Russell's table²⁴ for -0.77 ± 0.02

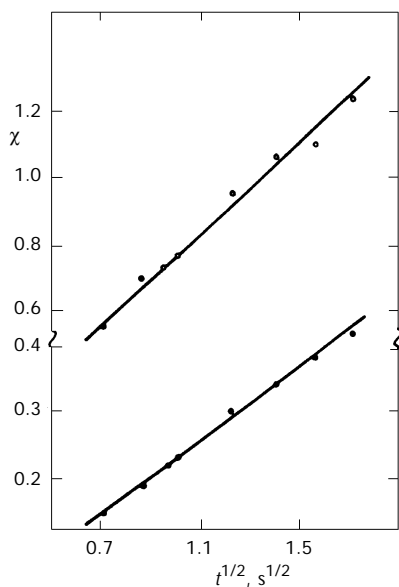


FIG. 4

Dependence of χ on the drop time for the first prewave (●) and the second prewave (○). $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

and -0.97 ± 0.02 V (vs SCE), *i.e.* the first and second prewaves, respectively. These potentials correspond to the limiting currents of both prewaves. From $\ln \chi_{II}$ vs Ψ^0 plot, charge of $+0.60$ was found for the PAC responsible for the second prewave. However, no evidence of a Ψ -effect was found for the first prewave (Fig. 5). This fact itself cannot prove the origin of the prewave, since for a surface process and sum of ion charges equal to zero, χ should not significantly depend on the Ψ -potential^{18b}.

It is well known²⁵ that an increase in the concentration of surface-active anions in the supporting electrolyte gives rise to limiting currents of prewaves. We have confirmed²⁶ adsorption of NO_3^- on the DME which obeys Langmuir's isotherm. The specific adsorption is modifying the double-layer structure and, consequently, the potential on the outer Helmholtz plane. Bockris *et al.* have shown²⁷ that the adsorption of NO_3^- is not important at concentration below 0.5 mol dm^{-3} , hence it has little effect on the magnitude of Koutecký's parameter. The only relevant effect of anionic species appears to be on the charge of the polarographically active compound (PAC) possibly due to the association of Ni^{2+} species with anions in the surface layer. On the other hand, the effect of cations on χ value is noticeable only for the second prewave¹⁰ as a result of specific cation adsorption because the second prewave is not located in the vicinity of p.z.c.

The temperature dependence of χ allows the determination of both the activation enthalpy ΔH^\ddagger and activation entropy ΔS^\ddagger at $c_{\text{Ni}^{2+}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$,

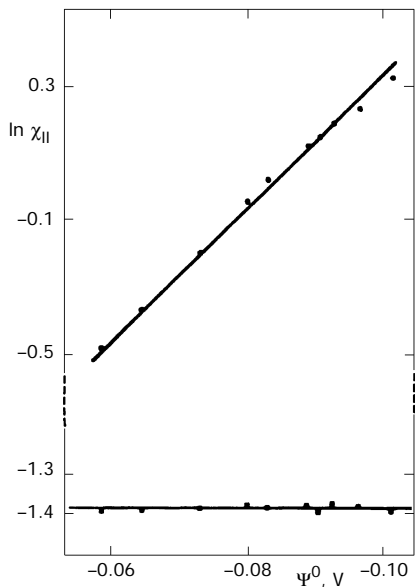


FIG. 5
Dependence of χ on the potential of the Helmholtz plane for the first prewave (●) and the second prewave (○), $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

$I(\text{KNO}_3) = 0.2 \text{ mol dm}^{-3}$, pH 6.0, and $t = 1.5 \text{ s}$ (Table III). The existence of a compensation effect was confirmed, and then the isokinetic temperature T^{iso} was determined, being 262.6 K ($r = 0.9980$) and 287.8 K ($r = 0.9998$) for the first and second prewaves, respectively.

Changes of $E_{1/2}$ with the drop time t indicated the irreversibility of the electrode process. Consequently the irreversibility of the polarographic curve was analyzed. Plots of $\ln i/(i_d - i)$ vs $-E$ for different SCN^- concentrations are given in Fig. 6. Their hyperbolic profile is characteristic of a quasi-reversible process²⁸. From the Koryta's criterion²⁹, extrapolation of the first part of the plot allowed to obtain the values of $E_{1/2}$ for reversible conditions. From the slope of the same plot, the number of electrons n which participate in the charge transfer process, was determined at $c_{\text{Ni}^{2+}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $T = 298.15 \text{ K}$, pH 6.0, and $t = 1.5 \text{ s}$ (Table IV). Moreover, from the second part of the plot, both the transfer coefficient α and $\Delta E_{1/2} = (E_{1/2}^{\text{irrev}} - E_{1/2}^{\text{rev}})$ were obtained. Table IV summarizes all these results, allowing to conclude that $\alpha = 0.5$ and $n = 1$ for the first prewave.

TABLE III
Activation parameters^a

Prewave	$c_{\text{SCN}^-} \cdot 10^2, \text{ mol dm}^{-3}$	$\Delta H^*, \text{ kJ mol}^{-1}$	$-\Delta S^*, \text{ J K}^{-1} \text{ mol}^{-1}$
First prewave	0.80	3.810	250.62 (0.9964) ^b
	1.50	7.870	228.11 (0.9993)
	2.00	16.95	195.48 (0.9990)
	2.50	21.05	179.62 (0.9992)
	3.00	26.23	160.54 (0.9986)
	3.50	31.13	142.42 (0.9996)
Second prewave	0.80	2.720	245.60 (0.9985)
	1.50	5.230	231.75 (0.9982)
	2.00	27.91	154.81 (0.9987)
	2.50	33.22	135.19 (0.9997)
	3.00	52.84	68.58 (0.9961)
	3.50	59.50	45.81 (0.9998)

^a Experimental conditions: see the text. ^b Linear correlation coefficients.

TABLE IV
Analysis of the irreversibility of the first prewave^a

$c_{\text{SCN}^-} \cdot 10^2, \text{ mol dm}^{-3}$	$c_{\text{KNO}_3} \cdot 10^2, \text{ mol dm}^{-3}$	n	α	$-\Delta E_{1/2}, \text{ mV}$
0.4	0.1	1.04 (0.9911) ^b	0.48	62
	0.2	1.08 (0.9947)	0.48	71
	0.4	1.25 (0.9988)	0.41	69
0.8	0.1	1.02 (0.9983)	0.42	38
	0.2	1.07 (0.9982)	0.41	57
	0.4	1.13 (0.9990)	0.51	44
2.0	0.1	0.93 (0.9994)	0.48	15
	0.2	0.78 (0.9984)	0.63	24
	0.4	1.03 (0.9995)	0.58	23

^a Experimental conditions: see the text. ^b Linear correlation coefficients.

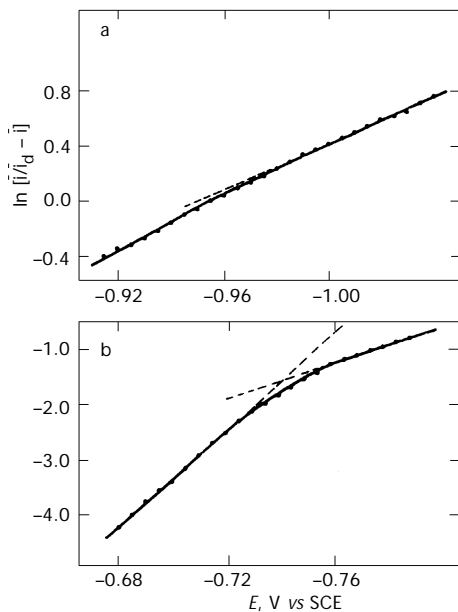


FIG. 6

Analysis of the irreversibility of the polarographic curve for the first (b) and second prewave (a). $c_{\text{Ni(II)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.2 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

The method described by Bard and Faulkner³⁰ was used to obtain the exchange current i_0 . The plots of $\ln(i_d - \bar{i})/\bar{i}$ vs η (overpotential) are linear in the Tafel region (correlation coefficients $r > 0.99$). From the intercepts, i_0 values were obtained. The plots of $\ln i_0$ vs $\ln c_{\text{Ni}^{2+}}$ were linear (Fig. 7) for the first prewave, second prewave and main diffusion wave with the slope close to 1.0.

In the region $\eta \rightarrow 0$, the stoichiometric number $\nu = 1$ was determined from η vs i plots for the first prewave at $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $T = 298.15 \text{ K}$, pH 6.0, and $t = 1.5 \text{ s}$ (Table V). For the second prewave the dependence of η vs i was not sufficiently accurate.

TABLE V

Values of the stoichiometric number, n , for the first prewave^a

$c_{\text{Ni}^{2+}} \cdot 10^2, \text{ mol dm}^{-3}$	ν/n
1.0	0.93 (0.9979) ^b
3.0	0.93 (0.9975)
4.0	0.91 (0.9968)
6.0	0.93 (0.9975)

^a Experimental conditions: see the text. ^b Linear correlation coefficients.

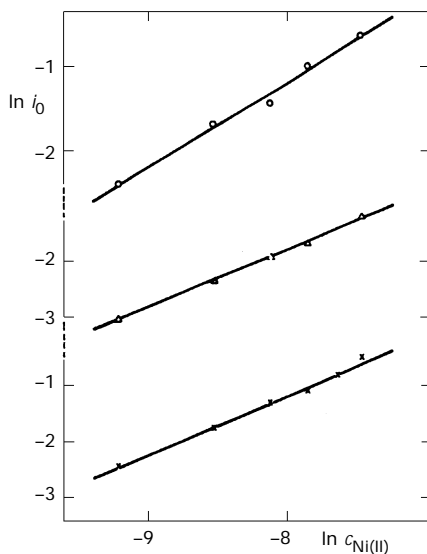


FIG. 7

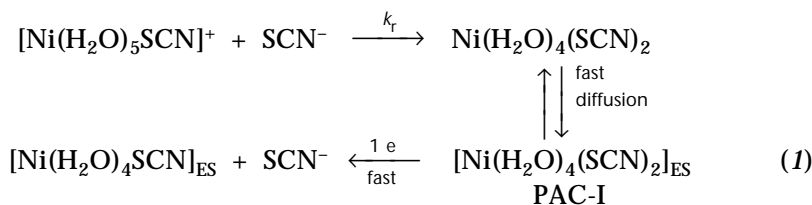
Dependence of the exchange current on the Ni(II) concentration for the main wave (\times), the first (Δ) and second prewave (\circ). $c_{\text{SCN}^-} = 8.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.2 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

Formal Mechanism

The dependence of χ_{II} (second prewave) on SCN^- concentration shows that the charge transfer is not the rate-determining step for the second prewave, but it corresponds to the surface process. An $E-t$ plot (Fig. 3), together with the dependence of χ_{II} on cationic species in supporting electrolyte represent additional proofs¹⁰.

According to our findings the first prewave is controlled by the reaction in the solution. In this work, the SCN^- concentration was not sufficiently low to suppress the formation of Ni^{2+} complexes. When the SCN^- concentration exceeds 0.1 mol dm^{-3} , Ni^{2+} can form up to three different thiocyanate complexes NiSCN^+ , $\text{Ni}(\text{SCN})_2$ and $\text{Ni}(\text{SCN})_3^-$ (ref.⁵). Galus and Jętic² have reported three waves corresponding to the reduction of $\text{Ni}(\text{SCN})_3^-$, NiSCN^+ , and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. They proposed that the wave at the most positive potential is due to the reduction of the $\text{Ni}(\text{SCN})_3^-$ complex. This assumption is not in agreement with Turyan's and Malyavinskaya's experimental data^{9a} which indicate formation of $\text{Ni}(\text{SCN})_2$ as a rate-determining step. The rate of formation of $\text{Ni}(\text{SCN})^+$ and $\text{Ni}(\text{SCN})_2$ complexes was determined from the limiting current of the first prewave assuming that the process takes place in the solution^{9b}.

Our work supports the Turyan's and Malyavinskaya's formulation^{9b} with some additional considerations. At the SCN^- concentration in the range from $4.0 \cdot 10^{-3}$ to $4.5 \cdot 10^{-2} \text{ mol dm}^{-3}$, the $\text{Ni}(\text{SCN})_2$ complex^{9a} represents only about 2% of total SCN^- concentration. Taking this into account, the following mechanism is proposed to explain the origin of the first prewave.



(ES: Electrode Surface)

The one-electron step (Table IV) is in agreement with $\nu = 1$ (Table V). Aggarwal and Crow³¹ have found that the electrochemical reduction of Ni^{2+} complexes with heterocyclic ligands involves two electrons. This contrasts with e.g. Ni^{2+} -thiourea (ref.¹³), for which one-electron transfer was found. Reduction of the PAC-I on the electrode surface (Eq. (1)) produces unat-

tached ligand molecules immediately adsorbed on the electrode surface regenerating thus the original SCN^- anion. It implies a catalytic character of the first prewave. However, at concentrations of SCN^- above $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ the reduction of $\text{Ni}(\text{SCN})_3^-$ can be responsible for the prewave as proposed by Verma⁴.

Here the Koutecký's theory of polarographic kinetic currents can be applied with the assumption of $c_{\text{SCN}^-}/K_2 \ll 1$, where K_2 is the stability constant of the PAC-I. Thus the following equation can be derived³²

$$\chi_1 = \frac{i_k}{i_d - i_k} = \sqrt{\frac{12}{7} \frac{k_r t}{K_2}} \frac{c_{\text{SCN}^-}}{K_1 + c_{\text{SCN}^-}} \quad (2)$$

Here K_1 and K_2 are the stability constants of the NiSCN^+ and $\text{Ni}(\text{SCN})_2$ complexes, respectively, and k_r is the rate constant of the rate-determining step from Eq. (1). The χ_1 values are satisfactorily fitted by Eq. (2) (Fig. 8) which represents an additional support for the mechanism proposed.

For this system, activation entropy values are more negative than for Ni^{2+} -thiourea (ref.¹³) as expected for the rate-determining step of a reaction between two species with opposite charges. However, the value close to -2 cannot be attributed only to the rate constant, k_r , of the rate-determining step because in Eq. (2) both K_1 and K_2 also depend on the ionic strength, I .

Although our interest is focused on the two prewaves, a consideration on the processes connected with the main wave must be taken in order to justify the origin of the second prewave. The formal mechanism explaining the existence of the main wave¹³ consists of diffusion and partial dehydration

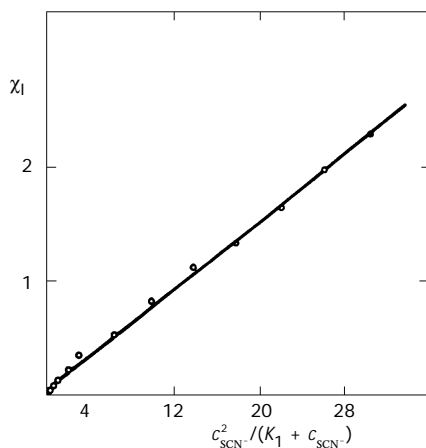
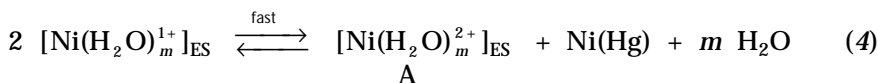
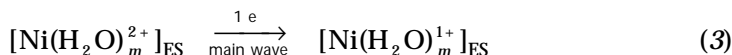


FIG. 8
Dependence of χ on $c_{\text{SCN}^-}^2 / (K_1 + c_{\text{SCN}^-})$ for the first prewave. $c_{\text{Ni(III)}} = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{KNO}_3} = 0.4 \text{ mol dm}^{-3}$, pH 6.0, $T = 298.15 \text{ K}$

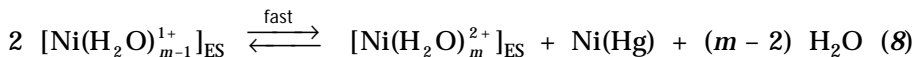
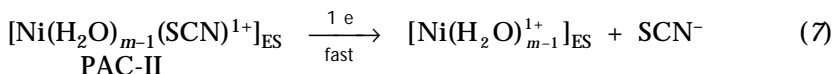
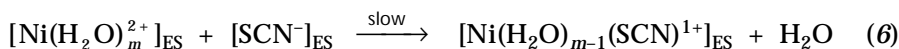
(acid catalyzed) of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, which yields $[\text{Ni}(\text{H}_2\text{O})_m^{2+}]_{\text{ES}}$ where $1 < m < 6$. Its reduction on the DME gives Ni(I) species, which is in agreement with our preceding results^{12,13} and also postulated by others³³.



For a compound formed from the adsorbate A and SCN^- Mark *et al.*³⁴ gave the following equation for the Koutecký's parameter:

$$\chi = k \theta_{\text{SCN}^-} \quad (5)$$

where θ_{SCN^-} is the surface concentration of SCN^- and k consists of number of parameters including the rate constant and the Ψ -potential. The results found for the dependence of the Koutecký's parameter χ_{II} on SCN^- concentration actually supports the Mark's formulation³⁴ for a ratio 1 : 1 between H_2O and SCN^- ligands in the adsorbed compound. The following mechanism for the second prewave can be proposed.



The deviation of the experimental value of charge (+0.6) from the theoretical value (+1) proposed for PAC-II represents an experimental error discussed above. The value +0.6 can be also a consequence of the NO_3^- effect

confirmed by the existence of $\text{Ni}(\text{H}_2\text{O})_5\text{NO}_3^+$ species³⁵. In this case, however, from the dependence of χ on NO_3^- concentration, their formation is not probable.

In the case of the second prewave, the kinetic salt effect points to a reaction of two species with opposite charges. On the other hand, the significant increase in the activation entropy compared with the first prewave (Table III) is consistent with both mechanisms and can be explained by higher complexing degree of SCN^- for the PAC-I than for the PAC-II compound.

The mechanism proposed for the second prewave is in agreement with its catalytic character which is only negligibly influenced by the adsorption¹⁰. It can be explained by the existence of adsorbed NiS which is formed^{5,6} from SCN^- and Ni^{2+} , both of them already adsorbed on the electrode surface. This process influences the mechanisms responsible for the prewave appearance^{7,8}.

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