ELECTROCATALYSIS OF HYDROGEN EVOLUTION BY TRANSITION METAL COMPLEXES

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Dedicated to the memory of the late Professor Antonín A. Vlček.

Voltammetric reduction of monothiocyanate complexes of the iron group metals is accompanied by catalytic evolution of hydrogen in two potential regions. Around –1.3 V *vs* SCE, hydrogen is evolved at the surface of the electrodeposited metal, around –1.6 V at the surface of mercury. The catalyst is the protonated reduced, zero-valent form of the complex which has limited stability. Minor differences in behaviour of the complexes of the three metals are due to different values of their complexation constant.
Keywords: Transition metals; Thiocyanate complexes; Electroreduction; Mercury electrode; Hydrogen catalysis; Electrolysis; Voltammetry; Polarography; Cobalt; Iron.

In his systematic research on polarography of complex compounds, Vlček paid special attention to the behaviour of zero- and low-valent transition metal complexes[1] and to their generation as products of electrode reactions[2–4]. When following the reduction of $[Ni(CN)_4]^{2-}$, he observed an accompanying formation of hydrogen bubbles at the electrode surface; in acid solutions, the front of the polarographic wave was overlapped by a maximum decreasing with increasing mercury pressure. Vlček found[2] that in acid medium, the primary reaction product, the zero-valent nickel complex $[Ni(CN)_4]^{4-}$, was partly oxidised to the parent complex and partly decomposed, yielding metallic nickel. It was evident that the low-valent reduction product was connected with the hydrogen evolution. These results, relevant to the catalytic evolution of hydrogen at the dropping mercury electrode (DME) in cobalt ion solutions containing thiols, the so-called Brdička reaction[5–7], led to the idea that in that reaction the catalyst is the zero-valent form of the pertaining cobalt complex. The Vlček's paper[4] has been since then often quoted in that connection[6,8–10].

When using hanging mercury drop electrode (HMDE) for their study of the Brdička reaction, Anzenbacher and Kalous described an additional process of catalytic evolution of hydrogen, manifesting itself as a peak on voltammetric curves in the potential range by some 300 mV more positive than the usual Brdička catalysis[11–13], which they denoted "peak P". Later on it was found[14–16] that this peak dramatically increases when the rate of potential scan slows down, and that the process is not confined to solutions of cobalt ions. The aim of the present communication is to introduce experimental data concerning the catalytic evolution of hydrogen on HMDE in the linear-scan (d.c.) voltammetric reduction of thiocyanate complexes of some transition metals, and to interpret the newly observed phenomena in agreement with the known facts about catalysis of electroreduction of hydrogen ion and with Vlček's results.

EXPERIMENTAL

Linear-scan voltammetric curves were recorded with the apparatus produced by the former Laboratorní přístroje Co., Prague: polarograph PA 4, electrode SMDE 1 in the HMDE function and *xy* recorder 4106. As auxiliary electrode, a small platinum foil was used, as reference electrode served a saturated calomel electrode (SCE); hence, the values of electrode potential mentioned below refer to SCE.

The solutions studied were prepared from bidistilled water and the following chemicals: $CoCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, KSCN, $Na_2B_4O_7$, $HClO_4$, CH_3COOH and NaOH, all of analytical grade. Before measurements the solutions were thoroughly deaerated by passage of pure nitrogen; during measurements nitrogen was passed above the solution in the cell.

RESULTS AND DISCUSSION

The experimental results reported below are limited to the effect of thiocyanate ion on the voltammetric reduction of cobalt(II), nickel(II) and iron(II) ions at the hanging mercury drop electrode; the concentration levels were kept within limits in which the corresponding monothiocyanate complexes $[M(SCN)]^+$ were prevailing[17]. It should be perhaps stressed that thiocyanate ion by itself is not electroactive in the potential range studied.

In Fig. 1, the d.c. voltammetric curves due to reduction of hydrated cobaltous ion in a borate buffer of pH 8.4 are shown, recorded with varied rate of potential scan. The two-electron electrode process is irreversible; under the given conditions, the peak current of electroreduction is controlled by diffusion. The presence of a small concentration of thiocyanate anion in solution changes the shapes of some of the curves, as can be seen in Fig. 2: at scan rates below 20 mV s^{-1}, a part of the curve at the foot of the peak
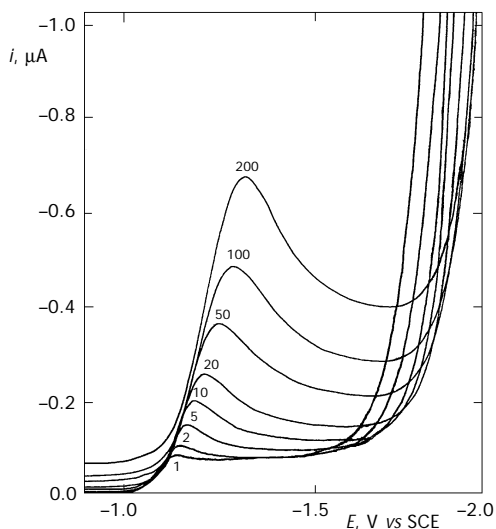
Linear-scan voltammetric reduction of $1 \cdot 10^{-1}$ mM $CoCl_2$ in $5 \cdot 10^{-2}$ M borate buffer of pH 8.4, recorded at various scan rates (denoted on the curves in mV s^{-1})
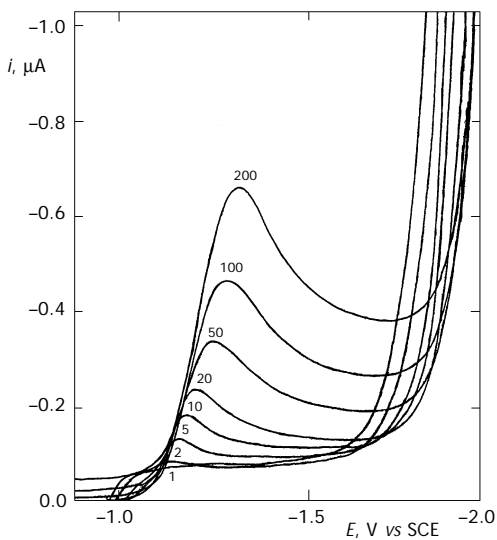
Solution as in Fig. 1, containing $9 \cdot 10^{-2}$ mM KCNS; the same dependence

shifts toward positive potentials – the slower the rate the more marked is the shift. Under the effect of ligands forming complexes with transition metal ions, the electroreduction of the original aqua-cations becomes faster and reduction curves are displaced in the positive direction. The ligands released in the course of electrode reaction react with the hydrated M(II) ions coming from the bulk solution and thus at the electrode new complexes are formed that readily undergo further electroreduction. This process, the so-called ligand catalysis, has been thoroughly studied (for the reaction of Co(II) with SCN⁻, see ref.[18]; for a general review see ref.[19]). According to the association constant of [Co(SCN)]⁺, the complex prevailing in dilute solutions of cobaltous and thiocyanate ions[20], the equilibrium bulk concentration of that complex in our case would be in the order of 10^{-7} mol l⁻¹ and its reduction would hardly show on the voltammetric curve, especially at low scan rates. The positive shifts of the lower parts of the curves at slow scan are due to slow adsorption at the negatively charged electrode of the positively charged thiocyanate complex ions and their ensuing surface catalytic reduction.

A different picture of the d.c. voltammetric reduction of cobaltous ions is obtained when the concentration of thiocyanate increases and the scan rate is varied (Fig. 3). The whole front of the reduction wave shifts now to posi-
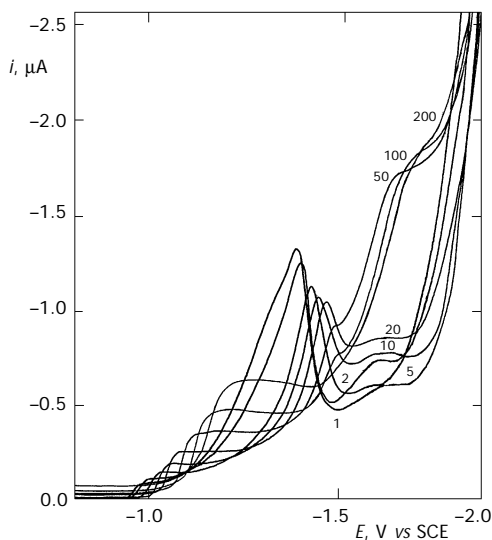

Fig. 3

Effect of various scan rates (denoted on the curves in mV s⁻¹) on d.c. voltammetric reduction of $1 \cdot 10^{-1}$ mM CoCl₂ in $5 \cdot 10^{-2}$ M borate buffer of pH 8.4, which is 9 mM in KSCN

tive potentials when the scan rate decreases indicating the importance of adsorption of the electroactive species from solution, and the steep increase in current points to the catalytic nature of the electrode process. The total height of the first reduction step is controlled prevailingly by diffusion. The curves recorded at relatively high-scan rates show a second, tall wave at negative potentials; at scan rates slower than 200 mV s^{-1}, a third wave appears between the two, that develops at 20 mV s^{-1} and slower scans into a prominent maximum that keeps steadily increasing. A voltammetric peak increasing with the decreasing scan rate is the sign of a catalytic process[15,21], analogously to the increasing current with decreasing mercury head in d.c. polarography[22]. The effect of different rates of individual phases of the electroreduction of the cobaltous thiocyanate complex on the outcome of the net reaction is demonstrated in Figs 4 and 5. When the electrode is polarised at the rate of 10 mV s^{-1}, the gradual addition of thiocyanate creates the positive shift of the first wave and the appearance of two maxima on its limiting current (Fig. 4). When, however, at the same solution conditions, the scan rate is increased ten times, the positive shift is hardly noticeable and only the more negative maximum appears at a
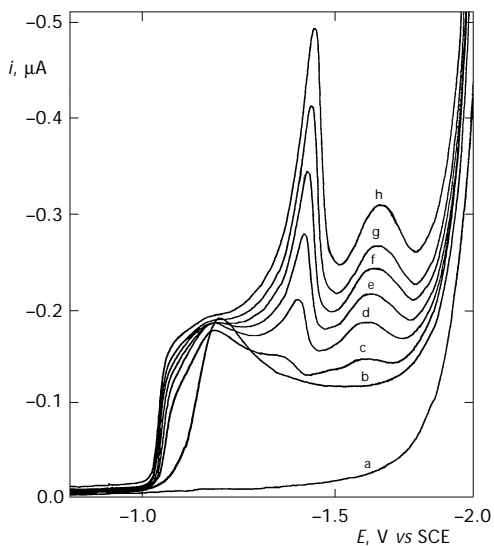

FIG. 4
Effect of additions of KSCN on d.c. voltammetric reduction of CoCl$_2$, scan rate v = 10 mV s^{-1}. Solution of $5 \cdot 10^{-2}$ M borate buffer of pH 8.4 (a), being $1 \cdot 10^{-1}$ mM in CoCl$_2$ (b); concentration of KSCN (in mmol l^{-1}): 1.1 (c), 2.1 (d), 3.2 (e), 4.2 (f), 5.2 (g), 6.2 (h)

higher thiocyanate concentration (Fig. 5). The relatively slow processes of adsorption accumulation and of the catalytic reaction producing the first maximum cannot come into play when the electrode potential is changing fast. Similarly, when recording d.c. polarographic curves with DME of 3 s drop-time in the same solutions as in Figs 4 and 5, virtually only the current due to the fast process of the second maximum appears at negative potentials.

Figure 3 resembles similar published pictures, showing the scan rate dependence of reduction d.c. voltammograms of cobalt(II) complexes with thiols[14–16]. There the first, more positive, maximum (the "P peak" of previous authors[11–13]) was interpreted as due to catalytic evolution of hydrogen by the cobalt complexes on electrodeposited metallic cobalt in distinction to the more negative maximum, where the hydrogen evolution is catalysed on mercury surface. In the first step, the reduction of the cobalt(II) complex, in our case of $[Co(SCN)]^+$, proceeds in the adsorbed state. The primary product of the two-electron transfer reaction, $[Co^0(SCN)]^-$, apparently slowly decomposes into cobalt atom and the SCN^- anion that gets involved in the ligand catalytic process. Atomic cobalt atoms aggregate into metallic cobalt, only slightly soluble in mercury[23]; Eriksrud[24] found that reduction
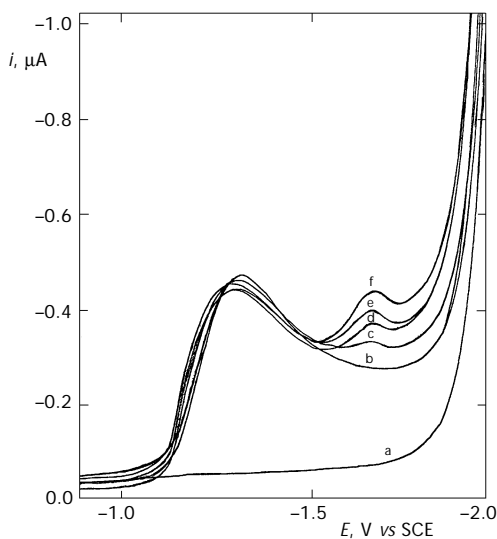

F_IG. 5
Effect of additions of KSCN on d.c. voltammetric reduction of $CoCl_2$, $v = 100$ mV s^{-1}. Solution of $5 \cdot 10^{-2}$ M borate buffer of pH 8.4 (a), being $1 \cdot 10^{-1}$ mM in $CoCl_2$ (b); concentration of KSCN (in mmol l^{-1}): 2.1 (c), 3.2 (d), 4.2 (e), 6.2 (f)

products on mercury electrode of $CoCl_2$ in thiocyanate solution are a composite film of amorphous cobalt sulfide and cobalt crystals. On metallic cobalt the electroreduction of hydrogen ions proceeds with considerably lower overpotential than on mercury[25,26]; the cobalt sulfide is possibly formed from cobalt thiocyanate in the course of hydrogen evolution on the cobalt surface. The actual catalyst of hydrogen evolution is presumably the reduced form of the cobalt complex, $[Co^0(SCN)]^-$, that, as a reduction product, gets preferentially protonated[27]. The protonation occurs, as obviously in catalysts of the Brdička reaction in general, at the sulfur atom bound to cobalt[28]. In the potential region of limiting current of the first reduction step, the surface concentration of the cobaltous thiocyanate is zero; it is supplied to the electrode by diffusion and the electron transfer does not occur at the electrode surface any longer, but the electrons tunnel to the electroactive species over a distance which increases with increasing negative potential[29]. Thus, the reduced product, the catalyst $[Co^0(SCN)]^-$, is formed in the solution near the electrode and its decomposition therein does not result any more in metallic crystals able to catalyse hydrogen evolution, but presumably in products of a slow reaction of the zero-valent complex with water. In that reaction, water appears as oxidising agent and the products are probably some mixed hydroxocomplexes of divalent cobalt that do not possess any longer catalytic ability. That is presumably the cause of decrease in the more positive catalytic current. In the course of continuing negative scan, the potential region is reached where the primary undecomposed reduction product, the zero-valent cobalt thiocyanate, in its protonated form, is able to catalyze hydrogen evolution on the surface of pure mercury; it can reach the surface from the site of its generation within its life-time. That situation gives rise to the second catalytic maximum; however, as the distance of electron transfer increases further, the catalyst undergoes the deactivation reaction before it can reach the electrode, and the second catalytic maximum decreases (Figs 4 and 5) or it merges with the increase in current due to reduction of the supporting electrolyte (Fig. 3). The reduced form of some complexes, when generated out of the contact with the electrode, obviously decomposes so fast that the second hydrogen catalytic process does not occur at all[13,15]. Whereas the appearance of the first catalytic peak on the voltammetric curve is conditioned by a complex heterogeneous process, the catalysis in the negative potential range consists in a mere short contact of the protonated catalyst with the mercury surface; hence the latter net catalytic reaction is faster than the former, as it follows from the above experimental curves. The great difference in the second catalytic current when the voltammetric

curve is recorded at the rates of 50 and 20 mV s^{-1} (Fig. 3) can be explained by the inhibitive action of the inactive products of the first catalysis that occupy the electrode surface and hinder its contact with the freshly formed catalyst.

In acid solutions, where the proton competes with the cobaltous cation for the thiocyanate anion (HSCN is a relatively strong acid with $K_A = 0.142$ mol l^{-1}, ref.[30]), the effects of thiocyanate additions in the same concentration relations as in Fig. 4 are incomparably weaker. In a 0.1 M acetate buffer of pH 4.7 with scan rate of 10 mV s^{-1} and highest SCN$^-$ concentration, a slight increase in current appears at the foot of the first step, amounting to about 30% height of the limiting current; this increase totally disappears when the scan rate is increased to 100 mV s^{-1}. No effects due to catalytic evolution of hydrogen could be observed. Itabashi[31,32] obtained catalytic maxima in d.c. polarography of acidic solutions containing Co(II) and thiocyanate ions at higher concentration levels than in our experiment. The maxima occurred in the potential region corresponding to our first catalytic peak and they increased with increasing acidity; however, the author did not ascribe them to hydrogen evolution.

The value of the association constant of ferrous monothiocyanate, [Fe(SCN)]$^+$, is slightly higher than that of its cobalt counterpart[20] and the d.c. voltammetric curves of ferrous and cobaltous ions in presence of thiocyanate ions are similar. Figure 6 shows the effect of the scan rate on the voltammetric reduction of ferrous ions in excess of thiocyanate ions. By comparing Figs 3 and 6, we can see that slow accumulation by adsorption of the ferrous complex also plays partly the role in ligand catalysis, and that when sufficient amount of the catalyst of hydrogen evolution, [Fe^0(SCN)]$^-$, is produced, the current due to hydrogen evolution appears. Its positive range, where hydrogen presumably evolves on the electrodeposited metallic iron, overlaps with the reduction peak of hydrated ferrous ion. To the same conclusions point also the curves in Fig. 7, analogous to Fig. 4; only the catalytic hydrogen evolution reactions are slower in the case of ferrous complexes. In acetate buffer, the additions of thiocyanate ion in the extent as in Figs 4 and 7 have no effect upon voltammetric reduction of ferrous ion.

The nickel(II) ion forms stronger monothiocyanate complex than cobalt and iron ions[17] and also the d.c. voltammetric results with Ni(II) are qualitatively different from those with Co(II) and Fe(II). The dependence of the voltammetric reduction of nickelous ions in excess of thiocyanate ions (Fig. 8) indicates that there is no slow accumulation preceding the catalytic onset of the electrode reaction by the ligand, and that the latter is not a
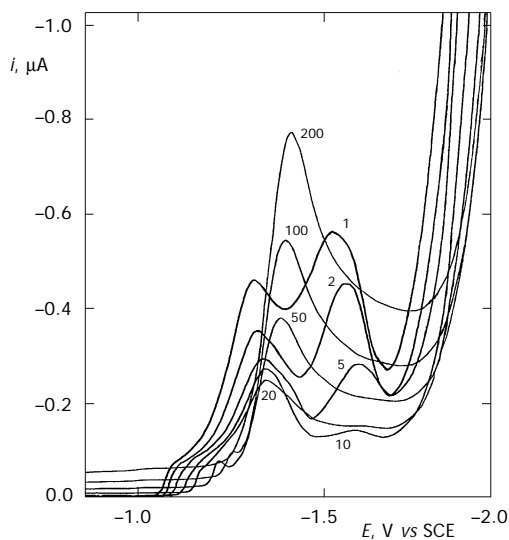
FIG. 6
Effect of the scan rate on d.c. voltammetric reduction of $1 \cdot 10^{-1}$ mM $FeSO_4$ in $5 \cdot 10^{-2}$ M borate buffer of pH 8.4, being 9 mM in KSCN. The scan rates are denoted on the curves in mV s^{-1}
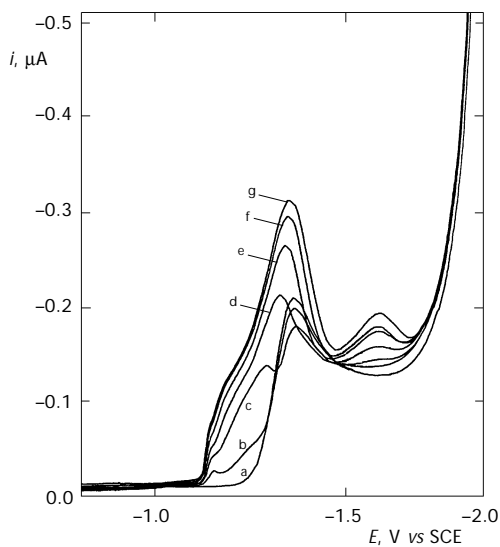

FIG. 7
Effect of additions of KSCN on d.c. voltammetric reduction of $FeSO_4$, v = 10 mV s^{-1}. Solution of $5 \cdot 10^{-2}$ M borate buffer of pH 8.4, being $1 \cdot 10^{-1}$ mM in $FeSO_4$ (a); concentration of KSCN (in mmol l^{-1}): 1.1 (b), 2.1 (c), 3.2 (d), 4.2 (e), 5.2 (f), 6.2 (g)
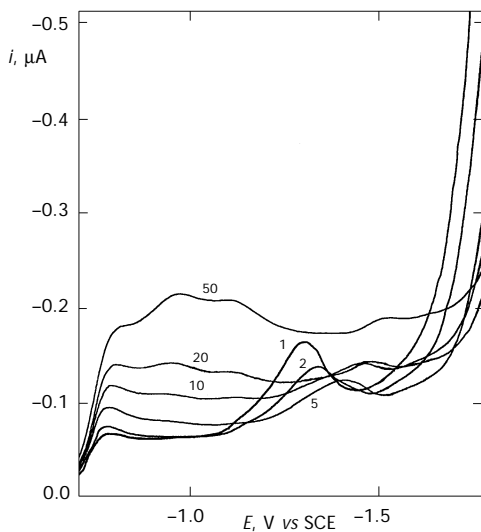
Fig. 8

Effect of the scan rate on d.c. voltammetric reduction of $1 \cdot 10^{-1}$ mM $NiSO_4$ in $5 \cdot 10^{-2}$ M borate buffer of pH 8.4, being 9 mM in KSCN. The scan rates are denoted on the curves in mV s^{-1}
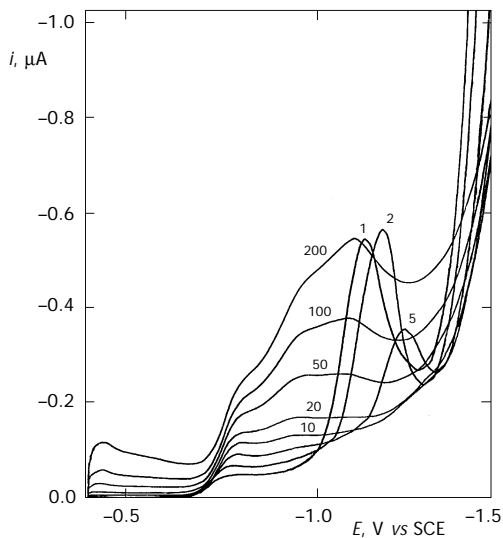

Fig. 9

Effect of the scan rate on d.c. voltammetric reduction of $1 \cdot 10^{-1}$ mM $NiSO_4$ in $1 \cdot 10^{-1}$ M acetate buffer of pH 4.7, being 6.2 mM in KSCN. The scan rates are denoted on the curves in mV s^{-1}

kinetically simple process. Only at the slowest scan rates, there appears a current peak of the faster of the two processes of catalytic hydrogen evolution on mercury, which lies at slightly more positive potentials than in the case of the complexes of the other ions. As a stronger competitor for thiocyanate ions than Co(II) or Fe(II) as compared with proton, the Ni(II) ion displays this type of hydrogen catalysis even better in acetate buffer solution (Fig. 9). On the voltammetric curves recorded at scan rate of 10 mV s^{-1}, addition of thiocyanate ions to Ni(II) solution in borate or acetate buffers shows the gradually developing ligand catalysis, but no hydrogen catalysis (Fig. 10).

CONCLUSIONS

The processes taking place in the course of electroreduction of monothiocyanate complexes of the iron group metals can be approximately described by the following reactions.

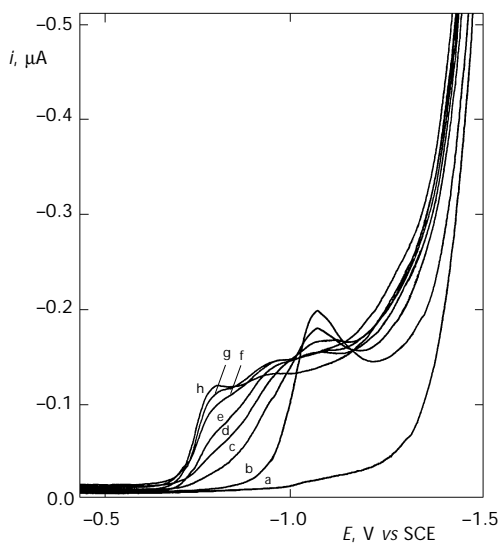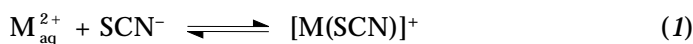– In the solution a relatively weak complex is formed (Eq. (*1*)).

$$M_{aq}^{2+} + SCN^- \rightleftharpoons [M(SCN)]^+ \qquad (1)$$

F IG. 10
Effect of additions of KSCN on d.c. voltammetric reduction of NiSO$_4$, v = 10 mV s^{-1}. Solution of $1 \cdot 10^{-1}$ M acetate buffer of pH 4.7 (a), being $1 \cdot 10^{-1}$ mM in NiSO$_4$ (b); concentration of KSCN (in mmol l^{-1}): 1.1 (c), 2.1 (d), 3.2 (e), 4.2 (f), 5.2 (g), 6.2 (h)
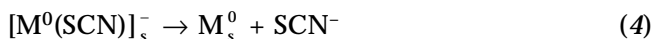
– The positively charged ion is adsorbed at the negatively charged electrode (Eq. (*2*)).
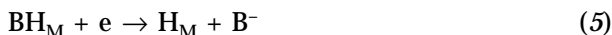
$$[M(SCN)]^+ \rightleftharpoons [M(SCN)]_s^+ \tag{2}$$

– The adsorbed complex undergoes a two-electron irreversible reduction (Eq. (*3*)).

$$[M(SCN)]_s^+ + 2e \rightarrow [M^0(SCN)]_s^- \tag{3}$$

– The reduction product with zero-valent metal partially slowly decomposes at the electrode surface (Eq. (*4*)).

$$[M^0(SCN)]_s^- \rightarrow M_s^0 + SCN^- \tag{4}$$

– At the deposited metal, atomic hydrogen is formed by electroreduction of the buffer (Eq. (*5*)).

$$BH_M + e \rightarrow H_M + B^- \tag{5}$$

– The undecomposed reduction product at the electrode surface gets protonated (Eq. (*6*)).

$$[M^0(SCN)]_s^- + H_s^+ \rightarrow [M^0(HSCN)]_s \tag{6}$$

– The protonated reduction product catalyses hydrogen evolution on the deposited metal (Eq. (*7*)).

$$[M^0(HSCN)]_s + H_M + e \rightarrow [M^0(SCN)]_s^- + H_2 \tag{7}$$
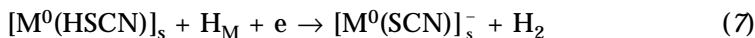
– At more negative potentials, the complex gets reduced in the non-adsorbed state (Eq. (*8*)).

$$[M(SCN)]^+ + 2e \rightarrow [M^0(SCN)]^- \tag{8}$$

– The zero-valent product partly decomposes (Eq. (*9*)).

$$[M^0(SCN)]^- \rightarrow products \tag{9}$$

– and partly gets protonated (Eq. (*10*)).

$$[M^0(SCN)]^- + BH \rightarrow [M^0(HSCN)] + B^- \tag{10}$$

– At negative potentials on mercury, atomic hydrogen is formed by electroreduction of the buffer (Eq. (*11*)).

$$BH_s + e \rightarrow H_s + B^- \qquad (11)$$

– When the protonated complex (Eq. (*10*)) reaches the electrode surface (Eq. (*12*)),

$$[M^0(HSCN)] \rightarrow [M^0(HSCN)]_s \qquad (12)$$

– it catalyses hydrogen evolution on mercury (Eq. (*13*)).

$$[M^0(HSCN)]_s + H_s + e \rightarrow [M^0(SCN)]_s^- + H_2 \qquad (13)$$
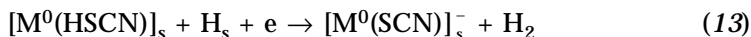
– When the catalyst gets out of contact with mercury, it decomposes (Eq. (*14*)).
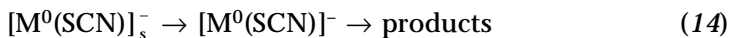
$$[M^0(SCN)]_s^- \rightarrow [M^0(SCN)]^- \rightarrow products \qquad (14)$$

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