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Polarographic Behavior of Nickel(II) in Propionitrile and Benzonitrile in the Presence of Thiocyanate Ions

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The effect of the cation of the supporting electrolyte on the electrode reaction of nickel(II) in propionitrile and benzonitrile solutions containing thiocyanate ion was investigated by DC polarography and *i-t* curve analysis. In the absence of thiocyanate ion, a propionitrile solution of nickel(II) gives a single irreversible wave in $LiClO_4$ and $NaClO_4$ supporting electrolytes and a double wave in Et_4NClO_4 and n-Bu_4NClO_4, and a benzonitrile solution of nickel(II) gives a double wave in alkali metal and quaternary ammonium perchlorates. Nickel(II) in these nitrile solvents in the presence of thiocyanate ion exhibits a catalytic pre-wave in alkali metal perchlorates and a catalytic maximum wave in quaternary ammonium perchlorates. The double wave of nickel(II) in the absence of thiocyanate ion is due to the inhibition of the charge transfer process by the relatively weak adsorption of quaternary ammonium cations and not to the presence of two electroactive species. A mechanism which involves the cyclic regeneration of adsorbed thiocyanate ion for the catalytic pre-wave and the catalytic reduction of thiocyanate ion with the electroreduced metallic nickel for the maximum wave has been presented.

The adsorption effect of the foreign substance on the electrode reaction in non-aqueous media has received less considerable attention, although that in aqueous media is well known. This could be the result of a weak adsorption of substance from non-aqueous solvents. Specific adsorption of quaternary ammonium cations from acetonitrile solution seems to be considerably weaker than from aqueous solution.

The electrode reaction of nickel(II) at the dropping mercury electrode in acetonitrile has previously been reported to be inhibited by the adsorption of quaternary ammonium cations[1] and to be accelerated by the adsorption of halide ions[2] as well as thiocyanate ions.[3] An acetonitrile solution of nickel(II) in the presence of thiocyanate ion exhibits two kinds of catalytic polarographic current.

Nickel(II) in $LiClO_4$ and $NaClO_4$ supporting electrolytes gives a catalytic pre-wave which arises at less negative potentials than that for the usual nickel(II) reduction wave, and in $(C_2H_5)_4NClO_4$ (Et_4NClO_4) and (n-$C_4H_9)_4NClO_4$ (n-Bu_4NClO_4) electrolytes a catalytic maximum wave over a wide range of potentials at which the usual nickel(II) reduction wave reaches its limiting plateau. It was proposed in a previous paper[3] that the electrode reaction mechanism for the maximum wave of nickel(II) was due to the catalytic reduction of thiocyanate ion with the electroreduced metallic nickel, and not to the catalytic hydrogen evolution.

In order to investigate the adsorption effect of quaternary ammonium cations on the electrode reaction of nickel(II) and the properties of the catalytic polarographic current of nickel(II) in the presence of thiocyanate and quaternary ammonium ions in non-aqueous solvents, some experiments were carried out in propionitrile and benzonitrile solvents. The present paper describes the experimental results on the above-mentioned systems.

Experimental

Purified propionitrile[4] and benzonitrile[5] were obtained by the procedures given in the literatures. All the other chemicals were prepared by the procedures described previously.[1,3] The total water content of the polarographic solution containing nickel(II) perchlorate and supporting electrolyte was found to be 10—20 mM by Karl Fisher titration. All solutions were *deaerated* with nitrogen gas. Direct current (D. C.) polarograms and current-time (*i-t*) curves of individual drops at constant potential were obtained with the potentiostat previously described[2] and made from operational amplifiers. In the following section and in the figures, "current" means them aximum current observed just before the fall of a mercury drop. The potential of the DME was measured against a saturated calomel electrode (SCE). The cell equipment for the polarographic measurements was the same as previously reported.[1] The dropping mercury electrode (DME) had an m value of 1.44_6 mg/sec and a drop time of 5.01 sec in a *deaerated* 0.1 M lithium perchlorate acetonitrile solution at −0.70 V *vs.* SCE and 60 cm mercury height. All measurements were made at 25.0±0.1°C.

Results

Propionitrile System. Larson and Iwamoto[4] have reported that a propionitrile solution of nickel(II) in 0.1 M Et_4NClO_4 supporting electrolyte gave an irregular reduction wave. The reduction wave of nickel(II) in propionitrile solution is influenced by the nature of the cation of the supporting electrolyte. The resultant polarograms are shown in Fig. 1. Nickel(II) gives an irreversible wave in $LiClO_4$ electrolyte and a double wave in Et_4NClO_4 and n-Bu_4NClO_4 electrolytes. A similar single reduction wave was also observed in 0.1 M $NaClO_4$ solution. Nickel(II) in alkali metal perchlorate solutions containing LiSCN gives a pre-wave, where it is reduced with greater reversibility. Figure 2 shows the effect of the thiocyanate concentration on the reduction waves of nickel(II) in $LiClO_4$ solution. The pre-wave increases in height

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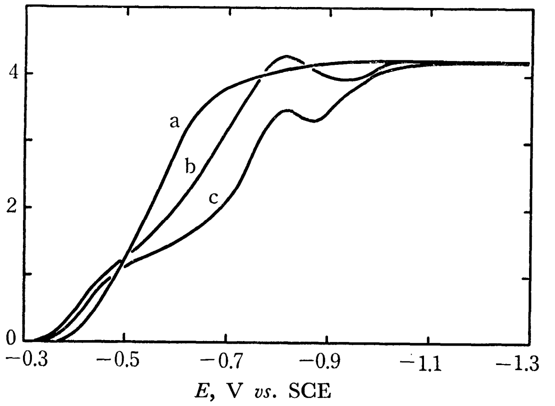

Fig. 1. Effect of electrolyte on the polarograms of 0.5 mM nickel(II) in propionitrile. (a), 0.1M $LiClO_4$; (b), 0.1M Et_4NClO_4; (c), 0.1M n-Bu_4NClO_4.

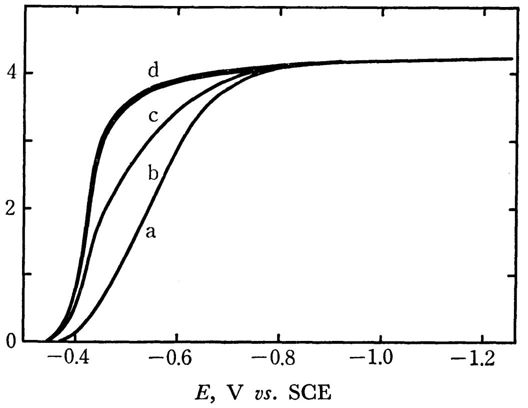

Fig. 2. Polarograms of 0.5 mM nickel(II) in propionitrile solutions containing 0.1 M $LiClO_4$ and various concns. of LiSCN: (a), 0; (b), 0.1 mM; (c), 0.3 mM; (d), 0.5 mM.

and becomes a more appreciable portion of the total limiting current of nickel(II) species as the thiocyanate concentration increases. There was no further essential change in the shape of the reduction wave when the thiocyanate concentration exceeded 0.5 mM. The effect of the thiocyanate concentration on the reduction waves of nickel(II) in n-Bu_4NClO_4 solution is shown in Fig. 3. Nickel(II) in n-Bu_4NClO_4 solution in the presence of small amounts of LiSCN exhibits a maximum wave over a wide range of potentials rather than a limiting plateau. The maximum wave increases in height with increase in concentration of LiSCN up to about 0.5 mM. Table 1 presents the exponents of the i-t curves for the reduction waves of nickel(II) in n-Bu_4NClO_4 solution containing various concentrations of LiSCN. The first step of the double wave of nickel(II) in the absence of LiSCN has a mixed diffusion-kinetic character, and the second step has the characteristics of normal diffusion control. In the presence of LiSCN, the exponents of the i-t curves for the maximum wave at the whole potential region examined are very close to the value of 0.67 expected for a kinetic-controlled electrode mechanism. The exponents of the i-t curves for the limiting current observed at the most negative potentials at which the maximum wave disappeared were found to be close to the value of 0.17 expected for a diffusion-controlled mechanism, whereas the limiting current of the pre-wave observed at potentials less negative than −0.5 V vs. SCE had a mixed diffusion-kinetic character.

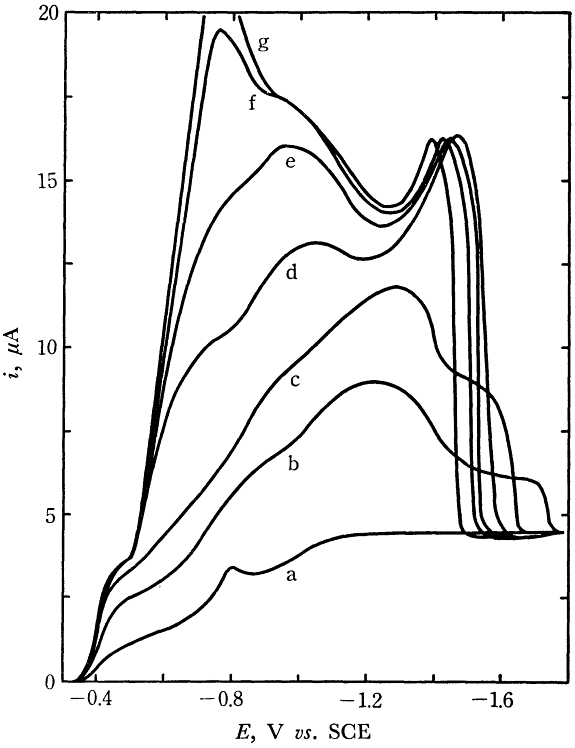

Fig. 3. Polarograms of 0.5 mM nickel(II) in propionitrile solutions containing 0.1 M n-Bu_4NClO_4 and various concns. of LiSCN: (a), 0; (b), 0.05 mM; (c), 0.1 mM; (d), 0.2 mM; (e), 0.3 mM; (f) 0.5 mM; (g), 1.0 mM.

TABLE 1. EFFECT OF CONCENTRATION OF LiSCN ON THE EXPONENT OF i-t CURVES FOR THE REDUCTION WAVES OF 0.5 mM NICKEL(II) IN 0.1 M n-Bu_4NClO_4 PROPIONITRILE SOLUTION

LiSCN mM	E V vs. SCE	x in $i_l=kt^x$	LiSCN mM	E V vs. SCE	x in $i_l=kt^x$
0	−0.50	0.53	0.5	−0.48	0.30
0	−1.20	0.19	0.5	−0.80	0.67
0.1	−0.48	0.27	0.5	−1.45	0.63
0.1	−1.20	0.60	1.0	−0.76	0.71
0.2	−0.48	0.27	1.0	−1.00	0.68
0.2	−1.00	0.61	1.0	−1.20	0.65
0.2	−1.46	0.64	1.0	−1.40	0.67

Benzonitrile System. The reduction wave of nickel(II) in benzonitrile has been investigated by Larson and Iwamoto,[5] who reported that nickel(II) gave a two-step reduction wave, and the second step was accompanied by a peak-type of maximum. Figure 4 shows the typical reduction waves of nickel(II) in benzonitrile containing various supporting electrolytes.

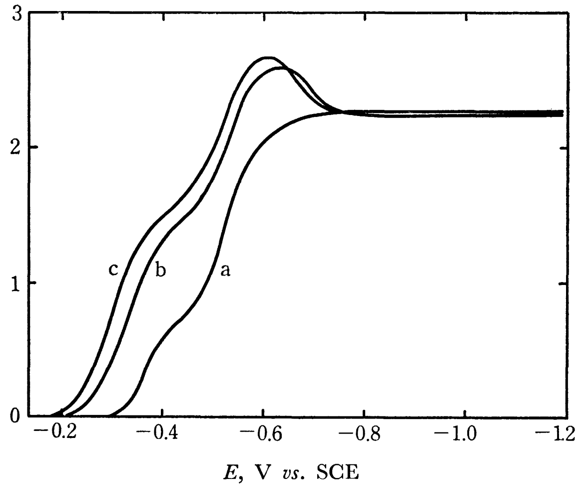

Fig. 4. Effect of electrolyte on the polarograms of 0.5 mM nickel(II) in benzonitrile. (a), 0.1 M $LiClO_4$; (b), 0.1 M Et_4NClO_4; (c), 0.1 M n-Bu_4NClO_4.

In any case, a two-step reduction wave was observed. The second step in quaternary ammonium percholrate solutions exhibits a round maximum at around −0.6 V *vs.* SCE. The limiting current of the first step was found to have a mixed diffusion-kinetic character from the results of the *i-t* curve measurements. In order to investigate the form of the electrocapillary curve, drop time measurements were made for benzonitrile solution. Drop time *vs.* potential curve exhibited a plateau in the potential region between −0.1 V and −0.7 V *vs.* SCE in 0.1 M $LiClO_4$ electrolyte solution, and irregularities which appeared as increase or decrease of drop time in the potential region between −0.2 V and −0.7 V *vs.* SCE in 0.1 M n-Bu_4NClO_4. Similar irregularities of drop time were also observed in benzonitrile solutions containing Et_4NClO_4, $C_6H_5N(CH_3)_3ClO_4$, and $C_6H_5CH_2N(CH_3)_3ClO_4$. The fact that drop time *vs.* potential curves in benzonitrile solution exhibits a slight irregularity has also been reported by Larson and Iwamoto.[5]

With small amounts of LiSCN present, the first step in $LiClO_4$ solution increased in height with increase in concentration of LiSCN. When the concentration of LiSCN exceeded 0.5 mM, the second step merged with the first step to give a single wave with the half-wave potential corresponding to the first step of the double wave. Figure 5 shows the effect of the thiocyanate concentration on the reduction waves of nickel(II) in 0.1 M n-Bu_4NClO_4 solution. In the presence of LiSCN, two maxima are observed in the potential region between −0.5 V and −1.5 V *vs.* SCE. The heights of the double maxima increase with increase in concentration of LiSCN up to about 1.0 mM. The limiting current observed at the most negative potentials at which the maximum wave disappeared was also enhanced by the presence of LiSCN. A similar enhancement of the limiting current at the most negative potentials was observed in benzonitrile solution containing the other quaternary ammonium perchlorates as supporting electrolyte. The resultant reduction waves are shown in Fig. 6. The increment of the limiting current caused by the addition of LiSCN was

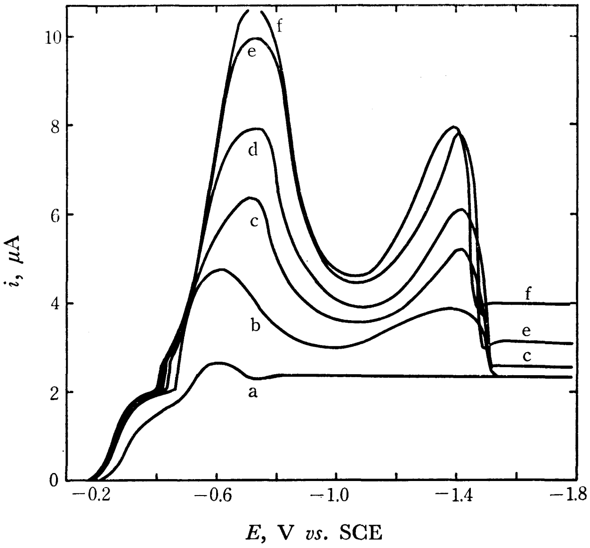

Fig. 5. Polarograms of 0.5 mM nickel(II) in benzonitrile solutions containing 0.1M n-Bu_4NClO_4 and various concns. of LiSCN: (a), 0; (b), 0.05 mM; (c), 0.1 mM; (d), 0.2 mM; (e), 0.5 mM; (f), 1.0 mM.

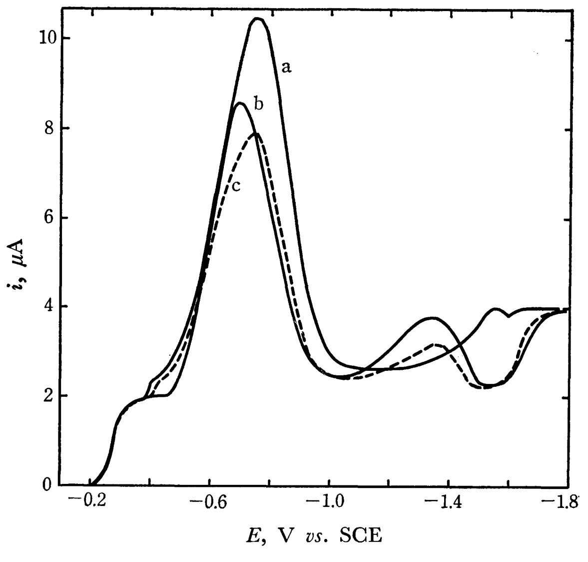

Fig. 6. Effect of electrolyte on the polarograms of 0.5 mM nickel(II) in benzonitrile solutions containing 1.0 mM LiSCN. (a), 0.1 M Et_4NClO_4; (b), 0.1 M $C_6H_5N(CH_3)_3ClO_4$; (c), 0.1 M $C_6H_5CH_2N(CH_3)_3ClO_4$.

TABLE 2. EFFECT OF CONCENTRATION OF LiSCN ON THE EXPONENT OF *i-t* CURVES FOR THE REDUCTION WAVES OF 0.5 mM NICKEL(II) IN 0.1 M n-Bu_4NClO_4 BENZONITRILE SOLUTION

LiSCN mM	E V *vs.* SCE	x in $i_1=kt^x$	LiSCN mM	E V *vs.* SCE	x in $i_1=kt^x$
0	−0.40	0.31	0.5	−1.10	0.63
0	−1.20	0.18	0.5	−1.76	0.18
0.1	−0.40	0.24	1.0	−0.78	0.65
0.1	−0.70	0.59	1.0	−1.38	0.66
0.1	−1.40	0.60	1.0	−1.76	0.18

found to be proportional to the concentration of LiSCN. Table 2 presents the exponents of the *i-t* curves for the reduction wave of nickel(II) in 0.1 M n-Bu_4NClO_4 solution in the presence of LiSCN. When the thiocyanate concentration exceeds 0.1 mM, the double maxima have the characteristics of kinetic control. While the exponents of the *i-t* curves of the limiting plateau observed at the most negative potentials are very close to the value of 0.17 expected for a diffusion controlled electrode mechanism.

Discussion

The double wave of nickel(II) in propionitrile and benzonitrile solutions containing quaternary ammonium cations could be explained by considering the adsorption of cations.

The kinetic property of the first step of the doublet is the result of the relatively weak adsorption of quaternary ammonium cations from nitrile solvents. The weakly surface active substance at consideravely higher concentrations causes the limiting current to decrease and also the drop life dependence of the instantaneous current to change[6,7] from $t^{1/6}$ to $t^{2/3}$. The appearance of the double wave in benzonitrile solution containing $LiClO_4$ is attributable to the adsorption of benzonitrile molecules on the mercury surface. Drop time *vs.* potential curve for benzonitrile solution containing 0.1 M $LiClO_4$ exhibited a plateau having no apparent change of drop time over a wide range of potentials at which the double wave of nickel(II) appeared. This finding could indicate the specific adsorption of benzonitrile molecules on the mercury surface. Benzonitrile differs from acetonitrile and propionitrile; it has delocalized electrons in the phenyl ring which are capable of interacting with mercury electrode.

The reaction mechanism of the pre-wave and the maximum wave for the nickel(II)-thiocyanate systems in propionitrile and benzonitrile can be written as the following sequence.[4]

$$\mathrm{Ni(NCS)^+} \overset{K}{\rightleftharpoons} \mathrm{Ni(II)} + \mathrm{NCS^-} \quad (1)$$

$$\mathrm{NCS^-}_{\mathrm{bulk}} \rightleftharpoons \mathrm{NCS^-}_{\mathrm{ads}} \quad (2)$$

$$\mathrm{R_4N^+}_{\mathrm{bulk}} \rightleftharpoons \mathrm{R_4N^+}_{\mathrm{ads}} \quad (3)$$

$$\mathrm{Ni(II)} + \mathrm{NCS^-}_{\mathrm{ads}} \xrightarrow{k_1} \mathrm{Ni(NCS)^+}_{\mathrm{ads}} \quad (4)$$

$$\mathrm{Ni(NCS)^+}_{\mathrm{ads}} + 2\,\mathrm{e} \xrightarrow[\mathrm{fast}]{} \mathrm{Ni(0)metal} + \mathrm{NCS^-}_{\mathrm{ads}} \quad (5)$$

$$\mathrm{Ni(0)metal} + \mathrm{NCS^-}_{\mathrm{ads}} \xrightarrow{k_2} \mathrm{Ni(II)} + \mathrm{CN^-} + \mathrm{S^{2-}} \quad (6)$$

where R_4N^+ refers to quaternary ammonium cation, K is the effective formation constant of the nickel(II)-thiocyanate complex in the bulk of the solution. k_1 and k_2 are the rate constants of reactions (4) and (6). The reactions (2) and (3) represent the adsorption equilibria of NCS^- and R_4N^+ ions, respectively. The cyclic regeneration of the adsorbed thiocyanate ion in the sequence of reactions (4) and (5) accounts for the catalytic enhancement of the pre-wave, and the cyclic regeneration of electroactive nickel(II) in the sequence of reactions (5) and (6) accounts for the catalytic process of maximum wave. The reaction mechanism of the maximum wave might be explained by considering the direct reduction of the adsorbed thiocyanate ion at the surface of electrodeposited nickel as the working electrode instead of reaction(6).

If the maximum wave is caused by the direct reduction thiocyanate ion at the deposited nickel, the height of the maximum wave would be close to the value of the diffusion controlled current to be expected. It is reasonable to postulate that the catalytic enhancement of the limiting current is due to the chemical reduction of thiocyanate ion with the deposited metallic nickel, and not to the direct reduction of thiocyanate ion at the deposited nickel.

The peaking of the catalytic current of the nickel(II)-thiocyanate system in the presence of quaternary ammonium cations could be the result of a slight polarographic maximum or it could indicate that the electrode reaction mechanism involves some adsorbed species. It is well known that the catalytic hydrogen waves of some organic sulfur-containing compounds and amines exhibit peaks which have been attributed to a mechanism involving adsorbed species.

Although this study has not provided any conclusive evidence as to the exact role of quaternary ammonium cations involved in the mechanism of the catalytic maximum wave, the fact that the catalytic maximum wave is observed in quaternary ammonium solutions and not in alkali metal solutions suggests that the nature of the electrodeposited metallic nickel is strongly dependent on the electrolyte present in the solution. If the reduction of nickel(II) proceeds at the part of the electrode covered with quaternary ammonium cations the amalgamation of the electrodeposited metallic nickel would be inhibited and the deposit remains on the surface of mercury electrode. The amalgamation of the electrodeposited iron-group metals in aqueous solutions is inhibited by the adsorption of several surface active substances.[8-10]

If the deposited metallic nickel in nitrile solvents in the presence of quaternary ammonium cations is an active species, it could react with thiocyanate ion. At the most negative potentials, the catalytic maximum wave disappears as a result of decreasing adsorption of quaternary ammonium cations and hence of decreasing concentration of the active metallic nickel. No appearance of the catalytic maximum wave of nickel(II) in alkali metal solutions is caused by the quick amalgamation of metallic nickel.

The limiting current observed at the most negative potentials in benzonitrile solution containing quaternary ammonium cations is enhanced by the presence of LiSCN. The total limiting current has the characteristics of normal diffusion control, and the increment of the limiting current caused by the addition of LiSCN is proportional to the concentration of LiSCN. The diffusion-current constant, I_D, for the increment

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of the limiting current was found to be nearly equal to the value expected for the one-electron reduction of various alkali metal ions in benzonitrile. When experiments were carried out using the benzonitrile solution containing 0.5 mM $(n\text{-}Bu_4N)_2Ni(NCS)_4$ and 0.1 M $n\text{-}Bu_4NClO_4$, the height of the limiting current at the most negative potentials at which the catalytic maximum wave disappeared was found to be equal to the magnitude of the diffusion current of nickel(II). Therefore, it is reasonable to postulate that the enhancement of the limiting current at the most negative potentials in benzonitrile solution containing quaternary ammonium cations is due to the discharge of lithium ions. The half-wave potentials of lithium ions in benzonitrile solutions containing 0.1 M $n\text{-}Bu_4NClO_4$ and 0.1 M $C_6H_5N(CH_3)_3ClO_4$ were found to be −1.80 V and −1.82 V *vs.* SCE, respectively. In the potential region where the specific adsorption of quaternary ammonium cations is absent, the electrodeposited metallic nickel is unstable and quickly amalgamates and reacts further with mercury to give the stable nickel amalgam. If a slight amount of deposited stable nickel still remains on the mercury surface in the potenital region where the catalytic maximum wave disappears in benzonitrile solution, this deposited nickel aids in reducing the overvoltage of lithium ions.

The reduction potential of sodium ions was also displaced towards less negative potentials in benzonitrile solution containing nickel(II), quaternary ammonium cations and NaSCN.

However, no apparent displacement of the reduction potentials of alkali metal ions was observed in acetonitrile and propionitrile solvents. This could be the result of the delocalized electrons in the phenyl ring of benzonitrile molecule facilitating electron transfer in the bridge mechanism of the electrode process.

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