Anomalous Electrode Behaviour of Aquonickel (II) Complex in Media containing Potassium Thiocyanate as Base Electrolyte

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Electro-reduction of aquonickel(II) complex in potassium thiocyanate as base electrolyte has been investigated at the dropping mercury electrode. A comparison of electrode behaviour has been made with that in other non-complexing media like KCl, KBr, KI, NaClO₄. The decrease in the half-wave potential value in thiocyanate medium is supported by an appreciable decrease in the activation energy of the electrode process. These anomalies together with facile electro-reduction have been explained by proposing a probable mechanism for the electrode reduction based on NCS⁻ bridge formation and a stereochemical change in the depolarizer structure. An anomalous ‘dip’, varying with KCNS concentration in the limiting current plateau observed has been explained on the basis of probable adsorption of nickel sulphide which may be formed at the electrode.

The study of kinetics and mechanism of electron transfer reactions of transition metal complexes at an electrode is an emerging field. Reaction pathways of a particular electron transfer reaction at an electrode may be totally different as compared to that in a homogeneous medium. The differences between the said two types of modes of redox processes have been recently resolved in a number of investigations and have been attributed to the specific properties of the electrode in question, adsorption of medium specis (electrolyte and ligand) at the electrode surface and the possible changes in the structure of the complex depolarizer prior to electron transfer. Isothiocyanate acts as a very modest catalytic bridging ligand in homogeneous electron transfer processes between transition metal centres, but it has been observed to be much more effective at mercury electrode surface for Ni (II) reduction. Ikeda and coworkers attributed the catalytic wave to the occurrence of a chemical reaction of freely deposited metallic nickel with thiocyanate, resulting in the formation of sulphides. This mechanism was questioned by Galus and coworkers. They explained the catalytic nature of the wave on the basis of the simultaneous reduction of thiocyanate ions and formation of sulphides and cyanides of nickel(II).

Thus a lot of emphasis has been given to the results of electro-reduction. If the products of the electro-reduction were the only driving force for an electrochemical reduction, thiocyanate should have catalysed all the electron transfer processes. However this has not been realised experimentally. The electrode behaviour of the aquonickel (II) complex in thiocyanate media is even now an open question. The purpose of this investigation is, therefore, to make an attempt to resolve this problem by studying the electrode behaviour of aquonickel (II) complex at dme in media containing potassium thiocyanate as the base electrolyte and compare the results with those of similar studies.

Materials and Methods

All the reagents used were of AR grade. Nickel was taken as nickel nitrate and its concentration was maintained at $2.5 \times 10^{-4} \text{M}$ in each case. Potassium thiocyanate of varying concentrations was used as the base electrolyte. Triton X-100 (0.001 %) was used as maximum suppressor in each case. Solutions were prepared in conductivity water and deaerated for 30 min. before recording the polarograms. The temperature was maintained at 25° ± 0.2°C in all the cases, unless otherwise stated.

Polarograms were recorded with a manual polarographic circuit recommended by Kolthoff and Lingane. The potentiometer (Leeds and Northrup) used was precise to ±0.1 mV and was powered by three dry cells (of 1.5V each). A box-type galvanometer (Rubicon Co., Philadelphia), precise to ±4 × 10⁻⁹ amp. was used. All potentials were measured against a Hume and Harris saturated calomel electrode (SCE). The cell resistance was measured with an a.c. wheatstone bridge and was found to be 1000 ± 100 ohms in almost all the cases. For this reason no correction of IR drop was necessary in these studies. Mercury for dme was purified first by chemical treatment with nitric acid, and then distilled twice under reduced pressure. The characteristics of dme determined in open circuit for 0.1M KSCN by noting the time for 50 drops with the help of a stop-watch precise to ±0.1 sec and then weighing were: $h = 40 \text{ cm}$, $t = 2.33 \text{ sec}$ , $m = 3.14\text{ mg sec}^{-1}$.

Results and Discussion

The current-voltage curves (Fig. 1) for electro-reduction of the aquonickel (II) complex at different concentrations of potassium thiocyanate as base electrolytes are found to be well-defined waves. At more negative potentials a peculiar drop in the diffusion current plateau is observed. This dip occurs beyond 0.1M concentration of potassium thiocyanate.
Fig. 1—Influence of varying KSCN concentration on aquonickel (II) (2.5 x 10^{-4} M) wave

Fig. 2—Dependence of $E_{1/2}$ for the reduction of aquonickel (II) complex (2.5 x 10^{-4} M) on the concentration of KSCN in the presence of 0.001% Triton X-100 at 25°C

and becomes broader and deeper up to 0.5 M KSCN. At higher concentrations, the area of the dip decreases and in 4.0 M KSCN, the dip disappears. These observations are in good agreement with the results obtained by Ikeda and Itabashi who also observed a one-step reduction along with a dip on the polarographic wave of nickel (II) at relatively negative potentials. But the investigations of Galus and Jefic for the same depolarizer at low thiocyanate concentration up to 0.01 M with 5 x 10^{-3} M Ni(II) show a three-step reduction.

The electrode behaviour characteristics ($E_{1/2}$, $i_d$, slope, transfer coefficient ($\alpha$) and $D^{1/2}$ of the polarographic (II) complex at varying concentrations of potassium thiocyanate (0.02 M-4.00 M) are given in Table 1. The $E_{1/2}$ values show a trend similar to that reported in literature. An examination of the data in Table 1 shows that the values of $E_{1/2}$ shift to more positive side with increase in [thiocyanate] and reaches a minimum (Fig. 2) at 0.50 M KSCN. At higher concentrations it shifts to more negative side. Similar observations were recorded by Tanaka et al. The values of the slope and transfer coefficient ($\alpha$) indicate that the process is irreversible at lower KSCN concentrations, but the reversibility increases with increasing KSCN concentrations. At 4.0 M KSCN (slope = 0.0346 and $\alpha = 0.86$), the process is almost reversible.

For the sake of comparison of the electroreduction of the aquonickel (II) complex in complexing (KSCN) and non-complexing (NaClO₄, KCl, KBr) media at 0.2 M concentration of the base electrolyte, the polarographic characteristics, along with activation energy, $Q_a$ calculated by Vlcek's method, are given in Table 2. It is seen that in complexing medium like KSCN, the aquonickel(II) complex undergoes electroreduction at a much more positive potential as compared to that in non-complexing media. This is also supported by the significant decrease in $Q_a$ values. Galus et al. have attributed the facile electroreduction to a complex formation of nickel (II) with thiocyanate and to the formation of NiS and Ni(CN)₄ due to simultaneous electroreduction of SCN⁻ ion. Such an interpretation is not compatible with the general observation that the electro-reduction of a complex having a ligand of stronger ligand field should be comparatively difficult. Weaver and Anson have advanced a bridge mechanism for such a facile electro-reduction of Eu(III) in thiocyanate solutions, as compared to that in bromide and iodide media which are less complexing, but are of nearly equally adsorbing nature. The facile electron transfer in Ni(II)-NCS system may
be understood on the basis of the formulation of a ligand bridge in which a thiocyanate ion is attached to both the electrode surface and Ni(II) in the transition state. Nickel (II) is known to form the complex \([\text{Ni(NCS)(H}_2\text{O)}_3])^-\) under present polarographic conditions. Electrostatic repulsion on such a negatively charged species at a slightly negatively charged electrode surface is overbalanced by this bridge formation. In fact, the complex species \([\text{Ni(NC}S]_2\text{H}_2\text{O)J}^-\), which may be assumed to be of octahedral stereochemistry and substitution labile nature, may get attached to SCN\(^-\) ion adsorbed\(^{18}\) at mercury and form a tetrahedral compound\(^{19}\), NiHg (SCN)\(_4\). In such a complex at mercury surface, NCS\(^-\) ion which has a system of \(\pi\)-bonds\(^{20-21}\) accelerates the rate of electron transfer from the electrode to the central metal ion.

The variation of the area of the dip occurring in the diffusion current plateau (Fig. 1) calls for special comments. Laitinen and Onstott\(^{22}\) observed a similar dip in the reduction of S\(_2\text{O}_3\)\(^2-\) ion. They explained it on the basis of electrostatic repulsion of the depolarizer anion at the negatively charged electrode in the region of dip potentials. Fujiwara and coworkers\(^{23}\) observed such a dip in the reduction of S\(_2\text{O}_3\)\(^2-\), PtCl\(_2\)\(^-\), CrO\(_4\)\(^2-\) etc. which they explained as arising out of some quantum mechanical effects. These explanations do not seem to be valid because at lower concentrations of the aquonickel (II) complex, in the present case, there is no dip in the plateau. It is, therefore, plausible to say that the origin of the dip may be in the adsorption of NiS which would be formed \(^{24}\) in the electro-reduction process at the electrode. At higher thiocyanate concentrations (say 0.5 \(M\) KSCN), the formation and adsorption of NiS would be maximum. At even higher concentrations, the adsorption of thiocyanate ion itself may overbalance the adsorption of NiS, and hence the decrease in the dip area resulting in its complete disappearance at 4.0 \(M\) KSCN.

**References**