Polarography of Tetracyano- and Dithiooxalato-Nickelate(II) Complexes[1]

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There have been no reports on the polarographic reduction of dithiooxalato-nickelate(II) complex, although some studies have been reported for tetracyano-nickelate(II) complex by several authors[2-8]. For instance, Hume et al.[6] studied the polarographic behavior of the tetracyanonickelate(II) ion and found that the ion, $[Ni(CN)_4]^{2-}$, is irreversibly reduced in one step and the wave corresponds to a two-electron reduction of the ion to metal. They also found that the univalent nickel complex ion, $[Ni_2(CN)_6]^{4-}$, is oxidized, but not reduced polarographically.

Recently, Vlček[7,8] studied the mechanism of the electrochemical reduction of the ion, $[Ni(CN)_4]^{2-}$, in further detail and obtained the following results. The electrochemical reduction of the ion, $[Ni(CN)_4]^{2-}$, proceeds principally by the acceptance of two electrons. The reduction product of the two-electron reduction may be either metallic nickel or a complex of zero-valent nickel, $[Ni(CN)_4]^{4-}$, the latter of which is very unstable in solution and is immediately oxidized to univalent nickel with evolution of hydrogen and simultaneous formation of the deep red ion, $[Ni_2(CN)_6]^{4-}$.

$$2[Ni(CN)_4]^{4-} + 2H_2O = [Ni_2(CN)_6]^{4-} + 2CN^- + 2OH^- + H_2$$

The ion, $[Ni_2(CN)_6]^{4-}$, is also oxidized to $[Ni(CN)_4]^{2-}$, though the rate is very small. The increase of the current in solution with a high concentration of the cyanide ion was explained as being due to the regeneration of bivalent nickel from the product of the electrode reaction.

The present paper deals with the polarography of the tetracyano- and dithiooxalato-nickelate(II) ions. The main purpose of this study is to examine polarographically whether the mixed complex is formed or not in the solution when the two kinds of ion, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, were mixed together.

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2) N. V. Emelianova, *Rec. trav. chim.*, **44**, 529 (1925).

3) G. Sartori, *Gazz. chim. ital.*, **66**, 688 (1936).

4) J. P. Hochstein, *J. Gen. Chem. U. S. S. R.*, **7**, 2488 (1937).

5) V. Caglioti, G. Sartori and P. Silvestroni, *Atti accad. natl. Lincei, Classe Sci. fis. mat. nat.*, **3**, 448 (1947).

6) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **72**, 4423 (1950).

7) A. A. Vlček, *Collection Czechoslov. Chem. Communs.*, **22**, 948 (1957).

8) A. A. Vlček, ibid., **22**, 1736 (1957).

Experimental

Apparatus.—A Yanagimoto model 104 polarograph with a sensitivity of galvanometer (2×10^{-9} μA/mm./m.) was used. For the determination of the half-wave potentials, the method previously described was employed[9]. An H-type cell with a saturated calomel electrode was used. The capillary used had a rate of flow of mercury, 0.635 mg./sec., and a drop time of 4.16 sec. in the solution of 1 F potassium chloride at an open circuit with a mercury head of 66.5 cm. The capillary was connected with a mercury reservoir by a tube of polyvinyl chloride. All the measurements were made at 28±0.1°C, the temperature being maintained by a water thermostat. The reversibilities of the electrode reactions were tested by determining the slope of $\log i/(i_d-i)$ vs. potential. Slopes of the log plots indicated irreversible reduction throughout.

Material. — The complex compounds studied were prepared by the following methods.

1. *Tetracyanonickelate(II) complx*, $K_2[Ni(CN_4]\cdot H_2O$. — Pure potassium tetracyanonickelate(II) complex was prepared in the usual way by dissolving freshly precipitated nickel cyanide in potassium cyanide and evaporating the filtered solution. On recrystallization from hot water, an orange crystalline product was obtained.

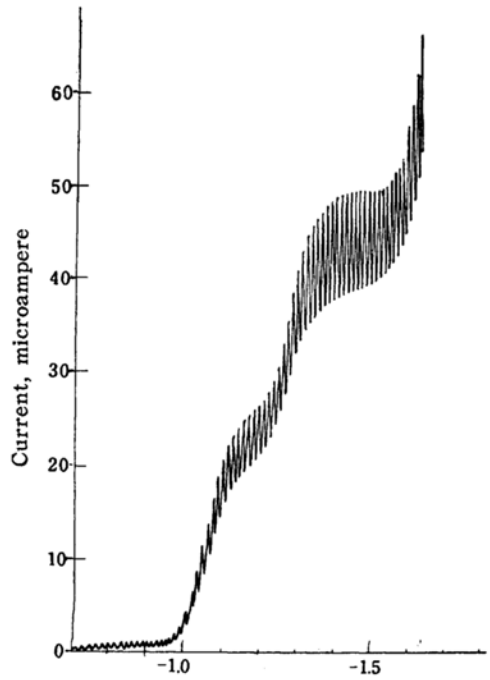
2. *Dithiooxalatonickelate(II) complex*, $K_2[Ni\cdot(C_2S_2O_2)_2]$[10,11]. — Concentrated aqueous solutions of nickel sulfate (2 g. in 10 ml.) and potassium dithiooxalate (2 g. in 4 ml.) were mixed at room temperature; a deep purple solution was at once produced, from which small, almost black crystals separated. The product prepared in this way is contaminated by the remaining simple salt and may be purified by recrystallization from hot water. After dissolving the crystals in water at 40°C, one-half its volume of the saturated solution of potassium nitrate was added to the solution, from which the large iridescent bipyramidal crystals separated again on cooling. The crystals were filtered and washed several times with water and ethanol; then they were transferred to a vacuum desiccator to remove the remaining ethanol.

The complex compounds used were checked for purity by the comparison of the ultraviolet absorption spectra. Each solution for electrolysis was made freshly from the dry crystalline nickelate(II) complexes before use. The solutions were mainly 0.005 F or 0.01 F with respect to the complex ion studied. In order to remove the dissolved oxygen, a vigorous stream of nitrogen which was purified from oxygen by means of an alkaline solution of pyrogallol was passed through the cell solution for an hour prior to each electrolysis, preventing the evaporation.

In order to examine the formation of the mixed complex, two kinds of solution of the same concentration for each ion were mixed together after the removal of the dissolved oxygen. After mixing, a stream of nitrogen was passed further for about ten minutes. Each polarographic run was completed within ten minutes. The maximum suppressor, Tween-80**, was added to the solution, which was enough to suppress the maxima of both the waves of the ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$. (0.0032% Tween-80). The supporting electrolyte used was 1 F potassium chloride.

Results and Discussion

The dithiooxalatonickelate(II) complex ion, $[Ni(C_2S_2O_2)_2]^{2-}$, is reduced irreversibly in two steps at the dropping mercury electrode in the solution of 1 F potassium chloride, as is shown in Fig. 1. The waves have a maximum at around −1.1 V. (vs. S. C. E.), which could easily be suppressed in the presence of 0.0032% Tween-80. The ratio of the height of the first wave to that of the second is approximately 1:1. This ratio is independent



Applied potential, volt vs. S. C. E.

Fig. 1. The polarogram of $[Ni(C_2S_2O_2)]^{2-}$ obtained at the concentration of 0.005 F in the presence of 0.0032% Tween-80. Supporting electrolyte; 1 F KCl. Temp., 28°C. Sensitivity; 0.400 μA/mm., Damping; 200. $E_{1/2}$ of 1st wave = −1.03 V., $E_{1/2}$ of 2nd wave = −1.25 V. vs. S. C. E.

9) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **30**, 909 (1957).
10) H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, **95**, 1904 (1909).
11) E. G. Cox, W. Wardlaw and K. C. Webster, ibid., **1935**, 1475 (1935).

** Polyoxyethylene sorbitan mono-oleate (Atlas Powder Co., in U. S. A.).

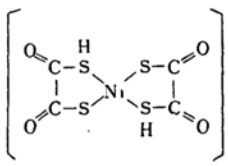
TABLE I. THE HALF-WAVE POTENTIALS AND THE CURRENT VALUES OF THE WAVES OF DITHIOOXALATONICKELATE(II) ION, $[Ni(C_2S_2O_2)_2]^{2-}$

Concn. of the ion (F)	$E_{1/2}$ of the 1st wave (V.)	$E_{1/2}$ of the 2nd wave (V.)	Total height of the waves (μA)
10^{-2}	−1.03	−1.25	80.0
5×10^{-3}	−1.03	−1.25	41.0
10^{-3}	−1.10	−1.31	20·8

1) The data obtained in the presence of 0.0032% Tween-80.
2) Supporting electrolyte; 1 F KCl.
3) Potential unit; V. vs. S. C. E., Temp., 28°C.
4) Characteristics of the capillary used; $m=0.635$ mg./sec., $t=4.16$ sec.

of the concentration of the complex ion. The limiting current for the unit concentration of the ion, i_l/c, becomes greater with the decreasing concentration of the ion. Table I shows the relation between the current value and the concentration. The fact that the heights of the waves of dithiooxalato complex are significantly greater than those of the usual nickel(II) complexes, such as $[Ni(CN)_4]^{2-}$, may well be explained as being due to the following reason. Namely, a part of the dithiooxalato complexes is considered to be present in solution as a form of the complex having protons to the sulfur atom.

For instance;



Hence, at the reduction potential of the complex, the hydrogen ion liberated from the complex is coreduced and contributes to the limiting current of the nickelate(II) complex. In conjunction with this consideration, the fact that the ratio of the height of the first wave to that of the second is always approximately 1:1 supports the idea that the dithiooxalatonickelate(II) complex might perhaps be reduced to the nickel(0) state in two steps. However, it appears desirable to delay further speculation on possible mechanisms of the reduction until more evidence, such as the data in buffer solution, is available. Concerning this point, further study is to be carried out in more detail and to be reported later.

On the other hand, the tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$, is reduced irreversibly in one step at the dropping mercury electrode in 1 F potassium chloride supporting electrolyte. (Fig. 2). The height of the wave is roughly proportional to the concentration of the complex ion. According to the results obtained by Vlček[7,8] and Hume et al.[6], the wave, corresponding to a gain of two electrons, represents the reduction for nickel(II) to nickel(0). In the solution of 1 F potassium chloride the wave of this ion indicated the maximum, which could be suppressed in the presence of 0.0016% Tween-80. In the solution of 0.5 F potassium sulfate it was very difficult to diminish the oxygen waves, which appeared at around −0.55 and −0.85 V. (vs. S. C. E.). Accordingly, the solution of 1 F potassium chloride was used as a supporting electrolyte to examine the formation of the mixed complex.

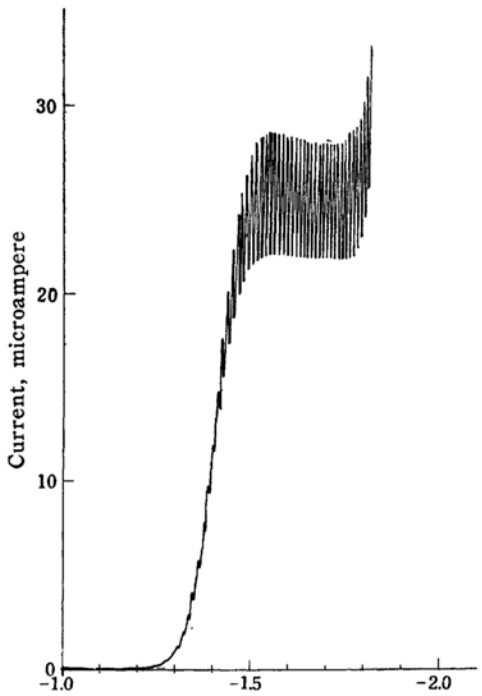


Fig. 2. The polarogram of $[Ni(CN)_4]^{2-}$ obtained in the solution of 1 F KCl at the concentration of 0.005 F in the presence of 0.0016% Tween-80. Sensitivity; 0.200 μA/mm., Damping; 200. $E_{1/2}=-1.38_5$ V. vs. S. C. E. $i_d=25.3$ μA.

In order to confirm the formation of the mixed complex, the solution of tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$, and of dithiooxalatonickelate(II) ion, $[Ni(C_2S_2O_2)_2]^{2-}$, are mixed together at each concentration of 10^{-2} F in the presence of

0.0032% Tween-80 after the removal of the dissolved oxygen. The polarogram of the mixed solution was taken within about a quarter of an hour after mixing. If the reaction between the complex ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, takes place, it is expected that the new reduction wave of the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, is obtained. This is neither the wave of the ion, $[Ni(CN)_4]^{2-}$, nor that of the ion, $[Ni(C_2S_2O_2)_2]^{2-}$. In fact, both the waves of the original ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, almost disappeared and a new well-defined wave was obtained near the potential between the waves of the original ions. This fact may be regarded as a proof for the formation of the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, in the solution. (Fig. 3).

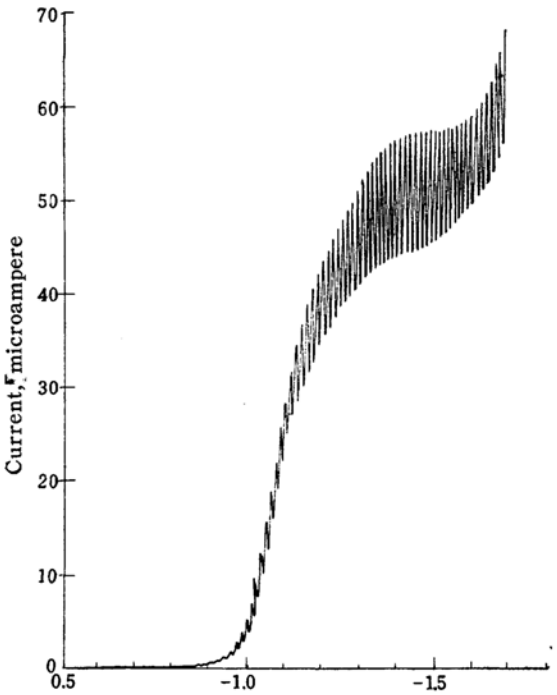
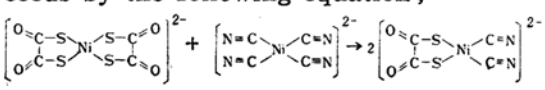


Fig. 3. The polarogram of the mixture of $[Ni(CN)_4]^{2-}$ and of $[Ni(C_2S_2O_2)_2]^{2-}$ at the equal concentration of 0.01 F for each complex ion obtained in the presence of 0.0032% Tween 80. The supporting electrolyte; 1 F KCl. $E_{1/2}$ of the wave $=-1.06$ V. vs. S. C. E. $i=47.6$ μA. Sensitivity; 0.400 μA/mm., Damping; 200.

It is considered that the reaction proceeds by the following equation;



The reaction was so fast that the progress of the reaction could not be detected nor traced by the classical polarographic method. The results obtained here are also supported by those of the spectrochemical study obtained by Kida[12].

The mixed complex ion, $[Ni(C_2S_2O_2)\cdot(CN)_2]^{2-}$, gives the irreversible wave of one step in the presence of 0.0032% Tween-80 in the solution of 1 F potassium chloride. The current is roughly proportional to the square root of the height of the mercury column. The straight line plot, however, does not pass through the origin but gives a negative intercept on the current axis. The height of the wave was not proportional to the concentration of the original ions. The half-wave potential of the wave shifts to the positive direction of potential with the decreasing concentration of the original ions.

For the same purpose as in the case of the dithiooxalatodicyanonickelate(II) complex, the polarogram of the mixed solution of the ions, $[Cu\ en_2^{***}]^{2+}$ and $[Cu\ ox_2^{***}]^{2-}$, was taken at equal concentration of both

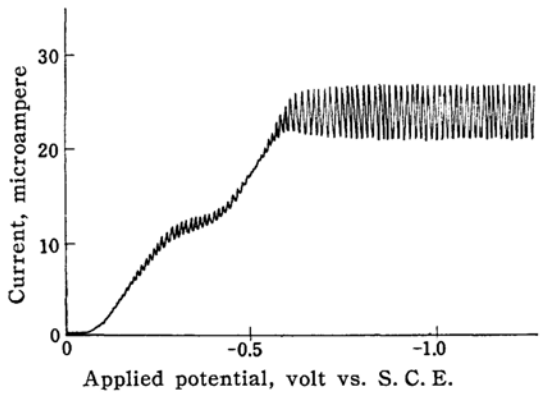


Fig. 4. The polarogram of the mixed solution of $[Cu\ ox_2]^{2-}$ and $[Cu\ en_2]^{2+}$ obtained in the presence of 0.0032% Tween-80. The supporting electrolyte used is 0.5 F $NaClO_4$. The mixed solution was prepared by mixing the solution of the same amount of $[Cu\ ox_2]^{2-}$ and of $[Cu\ en_2]^{2+}$ at each concentration of 0.005 F at 25°C. The half-wave potentials of both the waves were quite the same as those of the original ions, $[Cu\ ox_2]^{2-}$ and $[Cu\ en_2]^{2+}$.
$E_{1/2}$ of $[Cu\ ox_2]^{2-}=-0.14_5$ V. vs. S.C.E.
$E_{1/2}$ of $[Cu\ en_2]^{2+}=-0.49$ V. vs. S.C.E.
While the height of the wave becomes one half, since one is diluted to double by another.

12) S. Kida, This Bulletin, **29**, 805 (1956).
*** The following abbreviation was used; en=ethylenediamine, ox=oxalate.

the ions in the presence of 0.0032% Tween-80. (Fig. 4). In this case, however, the reduction waves obtained were only those of the original ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, and the wave of the mixed complex, [Cu en ox], could not be found, though the presence of this was verified by Kida[12] and DeWitt et al.[13] Namely, the percentage of the mixed complex formed in the solution is calculated to be 64%**** when equal amounts of both the ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, were mixed together at room temperature. This fact is explained as being due to the presence of the fast equilibrium among these complexes, $[Cu\,en_2]^{2+}$, $[Cu\,ox_2]^{2-}$ and [Cu en ox]. In other words, at the reduction potential of the ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, the equilibrium shifts very fast to the direction for supplying these ions. Further, in the equilibrium of the system,

$$[Ni(C_2S_2O_2)_2]^{2-} + [Ni(CN)_4]^{2-} \rightleftarrows 2\,[Ni(C_2S_2O_2)(CN)_2]^{2-}$$

its rate is very small. Consequently, the reduction wave of the mixed complex can be found. This fact suggests that the coordinating bond of these complexes has a considerable covalent character, in spite of the fact that the exchange reaction of tetracyanonickelate(II) ion with radioactive cyanide in solution is very fast[14].

13) R. DeWitt and J. Watters, *J. Am. Chem. Soc.*, **76**, 3810 (1954).
14) F. A. Long, ibid., **73**, 537 (1951).
**** The influence of temperature on the percentage is considered to be small.

Summary

1. It was verified polarographically that the reaction between the ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, takes place and the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, is formed in solution. The rate of the reaction was so great that the progress of the reaction could not be traced by the usual polarographic method. Meanwhile the wave of the oxalato-ethylenediamine copper(II) complex, [Cu en ox], the presence of which in solution had been verified spectrophotometrically, was not detected polarographically. That is to say, the polarographic method can be applied to detect the formation of the mixed complex, the coordinating bonds of which have a considerable covalent character, such as $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, but can not be applied to detect the mixed complex having ionic bonds.

2. The ion, $[Ni(C_2S_2O_2)_2]^{2-}$, is reduced irreversibly in two steps at the dropping mercury electrode in the presence of 0.0032% Tween-80, when 1 F potassium chloride solution was used as a supporting electrolyte. The heights of the two waves are not proportional to the concentration of the ion. The height of the wave for the unit concentration of the ion increases with the decreasing concentration of the ion.

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