The Formation of Complexes between Nickel(II) and Chloride Ions

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The formation of complexes between nickel and chloride ions has been studied at 25°C at an ionic strength of 4 M. The experimental data could be interpreted in terms of the formation of the complex $NiCl_2$. The corresponding stability constant was determined to be 0.13 M^{-2}.

The formation of nickel chlorido complexes has been investigated polarographically at 25°C at an ionic strength of approximately 2 M by Kivalo and Luoto,[1] who interpreted the results in terms of the formation of two complexes with the stability constants

$$\beta_1 = 0.56 \text{ M}^{-1} \qquad \beta_2 = 0.90 \text{ M}^{-2}$$

Lister and Rosenblum,[2] who used EMF methods at constant chloride concentration and an ionic strength of 2 M at 25°C, also found evidence for one, possibly two complexes, the stability constants of which were determined to be

$$\beta_1 = 0.57 \text{ M}^{-1} \qquad \beta_{21} = 0.41 \text{ M}^{-2}$$

By means of spectrophotometric methods at 5.7 M ionic strength, Netzel and Droll[3] detected one complex with a stability constant of

$$\beta_1 = 0.3 \text{ M}^{-1}$$

Tribalat and Caldero[4] also found evidence for one complex with a stability constant of

$$\beta_1 = 0.12 \pm 0.06 \text{ M}^{-1}$$

by means of spectrophotometric methods at 1.5 M ionic strength.

Other work in this field[6] involves ionic media or temperatures of little relevance to the present work.

EXPERIMENTAL

Three series of solutions were prepared from stock solutions of nickel chloride (*p.a.* Merck), nickel perchlorate, sodium chloride (*p.a.* Merck), and sodium perchlorate. The

nickel perchlorate was prepared from nickel carbonate (*p.a.* Merck) and perchloric acid (*p.a.* Merck) and recrystallized several times.

In each series the total nickel ion concentration (B) was kept constant, (B: 0.100, 0.200, 0.500 M), while the total chloride concentration (A) was varied between 0.200 and 2.150 M. The three series of solutions had the compositions given in Table 1.

Table 1. Values of Z and a for the nickel chlorido system.

$B = 0.100$ M

A	$\log a$	Z_{obs}	Z_{calc}
0.200	− 0.6990	0.000	0.010
0.450	− 0.3526	0.060	0.050
0.700	− 0.1624	0.120	0.115
0.950	− 0.0511	0.190	0.185
1.200	0.0682	0.300	0.299
1.450	0.1492	0.400	0.409
1.700	0.2070	0.520	0.502
1.950	0.2756	0.640	0.630

$B = 0.200$ M

A	$\log a$	Z_{obs}	Z_{calc}
0.400	− 0.4045	0.030	0.039
0.400	− 0.4089	0.050	0.039
0.650	− 0.2007	0.100	0.097
0.900	− 0.0635	0.180	0.176
1.150	0.0398	0.270	0.269
1.400	0.1236	0.355	0.372
1.650	0.1923	0.470	0.477
1.900	0.2514	0.580	0.582
2.150	0.3008	0.755	0.681

$B = 0.500$ M

A	$\log a$	Z_{obs}	Z_{calc}
0.250	− 0.6243	0.025	0.014
0.300	− 0.5474	0.035	0.021
0.375	− 0.4528	0.045	0.032
0.500	− 0.3325	0.070	0.054
0.750	− 0.1549	0.100	0.119
1.000	− 0.0434	0.190	0.119
1.250	0.0508	0.252	0.281
1.500	0.1226	0.348	0.370
1.750	0.1854	0.442	0.466
2.000	0.2396	0.528	0.560

The temperature was held constant at 25.0°C with a water thermostat and the ionic strength was held at 4.00 M by means of sodium perchlorate, the sodium perchlorate concentration being calculated according to the formula $4.00 - (2B + A^*) = [NaClO_4]$, where A^* is the concentration of chloride ions added as sodium chloride.

Solutions containing known total concentrations of nickel and chloride ions were allowed to run in 10 ml portions through a column filled with precipitated silver chloride labelled with $^{m110}AgCl(s)$ (half-life period = 253 days). Several samples were taken from each solution and the radioactivity was measured. This was repeated until the intensity became constant, at which point it was assumed that equilibrium had been attained. After passage through the column, the solution contained radioactive silver, since the solid silver chloride dissolved to form soluble silver chloride complexes with up to four ligands,[6] *i.e.* AgCl, $AgCl_2^{1-}$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$, besides likely nickel chloride complexes, *e.g.* NiCl$^+$ and NiCl$_2$. Mixed chloride complexes containing both nickel and

silver might also be formed. These ought, however, to be so weak compared to the $AgCl_n^{(n-1)-}$ complexes that their presence can be neglected. The total concentration of silver ions in the solutions is very low compared to that of both nickel and chloride ions and can therefore be neglected in the calculations. The total silver concentration is directly proportional to the radioactive intensity and is a function of the free chloride ion concentration only. A calibration curve of the radioactive intensity as a function of the chloride ion concentration was constructed from measurements on solutions containing no nickel ions. This was in good agreement with that obtained by Leden and Berne,[6] in which log[Ag] was plotted as a function of the free chloride ion concentration.

The radioactive intensity was measured with an electronic counter (PW 4032), an electronic timer (PW 4062), a high voltage supply (PW 4020), and a measuring cell (PW 4125/0) (Philips).

A correction was performed for the radioactive decay.

DETERMINATION OF POSSIBLE COMPLEXES

The concentration of free chloride ions ($[Cl^-] = a$) can be calculated from the solubility of silver chloride in the solutions (total concentration of silver in solutions in equilibrium with solid radioactive silver chloride).[7] Since the total nickel (B) and chloride (A) concentrations are known, the average co-ordination number (Z) could be calculated using the equation

$$Z = (A - a)/B$$

The average coordination number (Z) was then plotted as a function of log a and from this graph it was possible to obtain the values of β_1 and β_2 with a curve-fitting method, assuming the presence of two complexes only;[8] (Fig. 1). In the formulas b represents the free nickel ion concentration ($[Ni^{2+}]$).
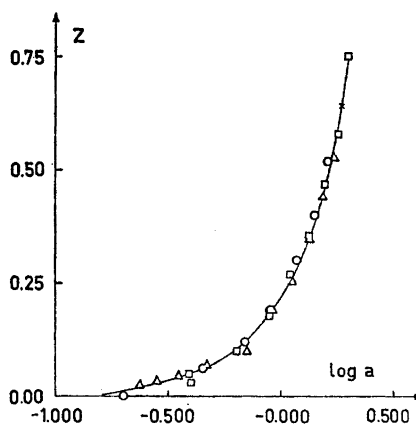

Fig. 1. Experimental values of Z vs. log a. The fulldrawn curve represents the normalized function $Z = f(\log u)$. $\times$ $[Ni^{2+}] = 0.100$ M; $\bigcirc$ $[Ni^{2+}] = 0.100$ M, coincident values from two measurements; $\square$ $[Ni^{2+}] = 0.200$ M; $\triangle$ $[Ni^{2+}] = 0.500$ M.

$$\beta_1 = [NiCl^+]/[Ni^{2+}][Cl^-] \qquad \beta_2 = [NiCl_2]/[Ni^{2+}][Cl^-]^2$$

$$Z = \frac{a + \beta_1 ab + 2\beta_2 a^2 b - a}{b + \beta_1 ab + \beta_2 a^2 b} = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2}$$

This function may be rewritten as

$$Z = \frac{Ru + 2u^2}{1 + Ru + u^2} \text{ where } R = \beta_1 \cdot \beta_2^{-\frac{1}{2}} \text{ and } u = a\beta_2^{-\frac{1}{2}}$$

The normalized curve for $R = 0.0$ fitted the experimental data well which indicated that there must be very little $NiCl^+$ present in the solution, $\beta_1 \approx 0$. The stability constant for the complex $NiCl_2$ was determined to be

$$\beta_2 = 0.126 \approx 0.13$$

The values obtained by the curve-fitting method were refined using the program Letagrop Vrid,[9] the final β_1 and β_2 values being:

$$\beta_1 = 0.000 + 0.015 \quad \beta_2 = 0.129 \pm 0.002$$

DISCUSSION

The β-values determined in this work differ from those found in previous investigations. In the most reliable of these investigations,[2] however, only one total chloride concentration was studied and the complex $NiCl_2$ could not of course, then be detected. If it is assumed that $NiCl^+$ only was present in our solutions, the corresponding β_1 value calculated from $\log \beta_1 = -(\log a)_{z=\frac{1}{2}}$ would be 0.63 M^{-1} as compared with 0.57 M^{-1}. In the remaining investigations polarography and spectrophotometry have been employed which would probably give less accurate results for this system.

Although the concentration of the complex $NiCl_2$, found in this investigation, is low, its existence seems to be well-established. The different Z-curves are independent of the total concentration of nickel in the interval 0.1—0.5 M, which excludes the possibility of polynuclear complex formation and means that the ionic medium is sufficient to prevent drastic variations in the activity coefficients.

The chemistry of nickel differs remarkably from the chemistry of palladium and platinum. It is, however, interesting to note that $PtCl_2$ is so stable that $PtCl^+$ has not been detected while the ratio β_1/β_2 which was found to be zero in the nickel system is about 3 in the palladium system.

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