

## Inorganic complexation of nickel and cobalt in natural waters

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**Abstract.** The distribution of nickel and cobalt species has been computed, based on the pH-dependent model of Zirino and Yamamoto. The media used in the pH range of 7 to 9 are natural waters like fresh water, sea water and a mixture of them at different compositions, at 25°C temperature and 1 atm pressure. In fresh water, both nickel and cobalt dominate as free cations at lower pH, and as carbonate complexes at higher pH. In sea water, chloro complexes are significant. In mixtures of the two kinds of water, as might be found in a totally mixed estuary, chloro complexes are important, varying slowly with pH. Sea water plays an important role in complexation. The present results are in excellent agreement with experimental data obtained by the resin exchange method.

**Keywords.** Nickel; cobalt; species pattern; pH; complexation; natural waters.

### 1. Introduction

Speciation calculations are of great significance in evaluating the fate of trace metals in biogeochemical cycles. In recent years, many theoretical and experimental studies have appeared on the equilibrium speciation of major and electrochemically active metals in natural waters. However, a few studies (Mantoura *et al* 1978; Turner *et al* 1981) are reported on the behaviour of trace metals in fresh and sea water media.

In this paper, we report the results of computations of per cent species of nickel and cobalt in natural waters like fresh water and sea water at 25°C temperature and 1 atm pressure, using a modified pH dependent model of Zirino and Yamamoto (1972) in the pH range of 7 to 9. This may help us in understanding the nature of the various complexes and their behaviour in natural waters. The calculations are further extended to mixtures of different compositions of fresh and sea water for observing the changes in the distribution of species in a completely mixed estuary.

### 2. Calculations

The model and appropriate mass balance equations used in the work are summarized elsewhere (Zirino and Yamamoto 1972; Long and Angino 1977). Thermodynamic equilibrium is assumed to exist and the pH range is 7 to 9 with an increment of 0.2. Since the concentrations of nickel and cobalt are very low, polynuclear and organic complexes are completely avoided (Helgeson 1969; Long and Angino 1977). Humic acid complexes are also avoided as their stability constants are presently unavailable as a function of pH. The speciation of major elements was calculated by the model of

Table 1. End numbers on molal scale used as input.

| Component                | Fresh water <sup>a</sup> | Sea water <sup>b</sup> |
|--------------------------|--------------------------|------------------------|
| Sodium                   | 0.000274                 | 0.4752                 |
| Potassium                | 0.000059                 | 0.01                   |
| Magnesium                | 0.000168                 | 0.054                  |
| Calcium                  | 0.000375                 | 0.0104                 |
| Chloride                 | 0.00022                  | 0.554                  |
| Sulphate                 | 0.000955                 | 0.0284                 |
| Effective ionic strength | 0.0021                   | 0.661                  |
| Total alkalinity         | 0.000955                 | 0.00234                |

<sup>a</sup>Livingstone 1963; <sup>b</sup>Berner 1971.

Table 2. Stability constants ( $\log \beta$ ) of various species of nickel and cobalt at 25°C.

| Species                       | $\log \beta$                               |
|-------------------------------|--|
| <i>Nickel</i>                 |  |
| Cl <sup>-</sup>               | $\beta_{11} = 0.73^a, \beta_{12} = 0.72^b$ |
| SO <sub>4</sub> <sup>2-</sup> | 2.32 <sup>b</sup>                          |
| HCO <sub>3</sub> <sup>-</sup> | 2.5 <sup>d</sup>                           |
| CO <sub>3</sub> <sup>2-</sup> | 5.37 <sup>c</sup>                          |
| OH <sup>-</sup>               | 4.16 <sup>b</sup>                          |
| <i>Cobalt</i>                 |  |
| Cl <sup>-</sup>               | 0.57 <sup>c</sup>                          |
| SO <sub>4</sub> <sup>2-</sup> | 2.36 <sup>b</sup>                          |
| HCO <sub>3</sub> <sup>-</sup> | 2.4 <sup>d</sup>                           |
| CO <sub>3</sub> <sup>2-</sup> | 4.91 <sup>c</sup>                          |
| OH <sup>-</sup>               | 4.15 <sup>b</sup>                          |

<sup>a</sup>Sillen and Martell 1964; <sup>b</sup>Sillen and Martell 1971; <sup>c</sup>Turner *et al* 1981; <sup>d</sup>Mantoura *et al* 1978.

Garrels and Thompson (1962). The compositions of fresh water and sea water used are listed in table 1. The ligands used for the complexation are OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> and their stability constants (Mantoura *et al* 1978; Turner *et al* 1981; Sillen and Martell 1964, 1971) are listed in table 2. Tables 1 and 2 are inputs of calculations. Stability constants were also critically examined by Turner *et al* (1981).

The activity coefficients of metals and their complexes are calculated by the Davies equation (Davies 1962) as

$$-\log \gamma_i = 0.5 z^2 [I^{1/2}/(1 + I^{1/2}) - 0.3 I], \quad (1)$$

where  $z$  is the charge on the ion and  $I$  is ionic strength. The use of MacInnes convention (MacInnes 1919) in calculating  $\gamma_i$  was avoided as it was not applicable to ionic strengths higher than 0.1. Activity coefficients of ion pairs (Reardon and Langmuir 1976) are given by

$$\log \gamma_{IP} = -BI \quad (2)$$

where  $B = 0.1, 0.3$  and  $0.5$  for 1-1, 1-2 and 2-2 ion pairs respectively and  $\gamma_{IP}$  is the activity coefficient of the ion pair. Activity coefficients of major ions are calculated from Robinson and Stokes (1959), using the mean salt method (Millero and Schreiber 1982). The hydration model of Bates (1978) was also attempted, which gave unrealistic  $\gamma_{Mg^{2+}}$  values and hence was dropped.

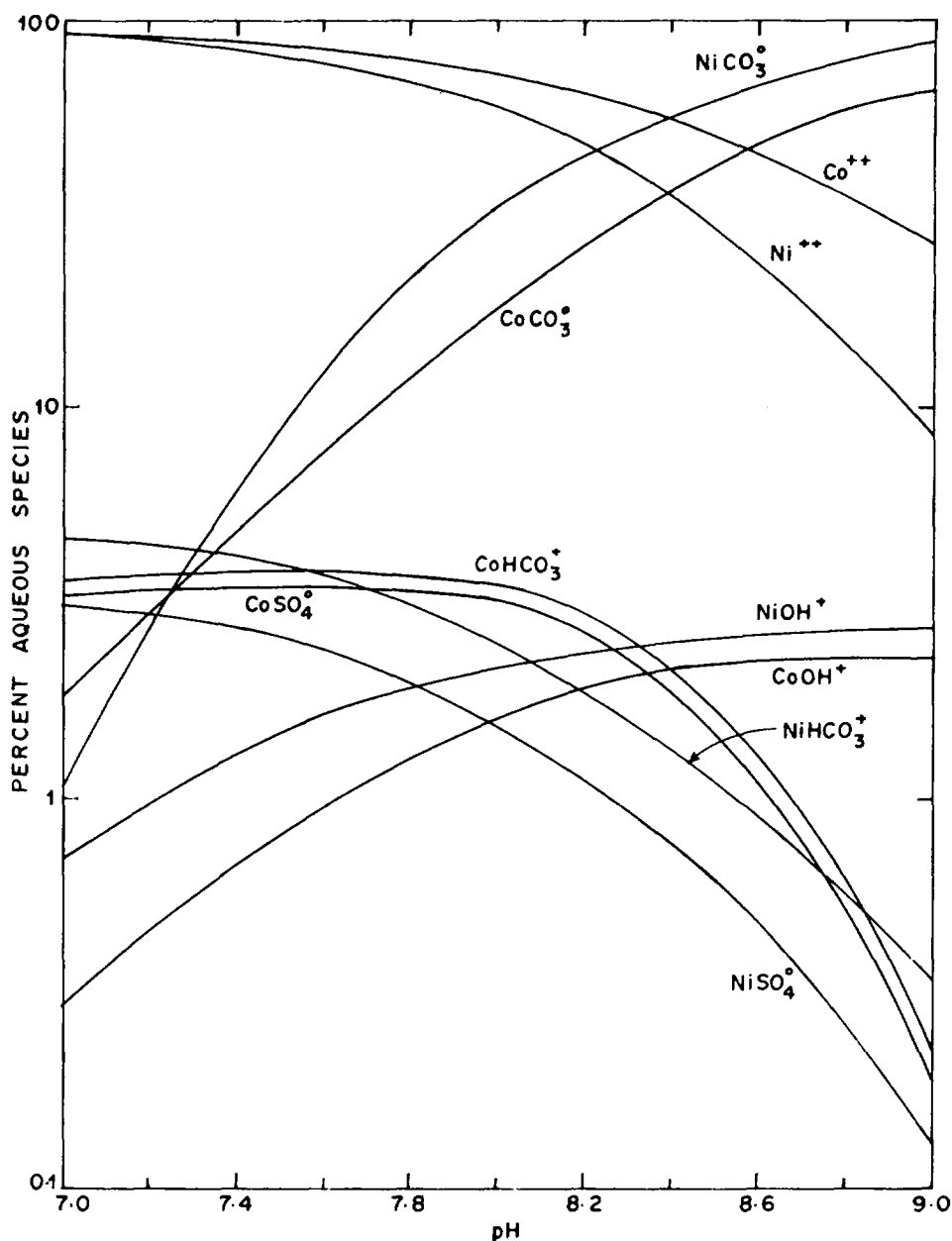


Figure 1. Inorganic complexation of nickel and cobalt in fresh water.

### 3. Results and discussion

The results obtained from computations are plotted as percent aqueous species (0.1 to 100%) on a log scale against pH. Distribution of different species of nickel and cobalt in 100% fresh water is shown in figure 1. Free  $\text{Ni}^{++}$  and  $\text{Co}^{++}$  both dominate upto pH 8.2, except that the magnitude of free  $\text{Co}^{++}$  is higher than free  $\text{Ni}^{++}$  as pH increases. Beyond pH 8.2, carbonato complexes dominate in both cases. Other complexes like sulphato, bicarbonato and hydroxy remain below 4% throughout. Table 3 shows a summary of values of percent of aqueous species of nickel and cobalt alongwith existing experimental and theoretical calculated values (Mantoura *et al* 1978; Turner 1981) for comparison.

In 100% sea water, both metals are complexed by about 50% in the forms of carbonato and chloro species. Figure 2 shows this fact, while table 3 compares our computed values at pH 8.2 of sea water. Present values at pH 8.2 for free Ni are slightly higher, otherwise the agreement is good. Unlike Turner *et al* (1981), the bicarbonato

Table 3. Chemical speciation (%) of nickel and cobalt in fresh and sea water.

| Species          | Fresh water |                           | Sea water<br>pH 8.2                           |
|------------------|-------------|---------------------------|---|
|                  | pH 7        | pH 9                      |   |
| <i>Nickel</i>    |             |                           |   |
| $\text{Ni}^{++}$ | 90.7        | 8.4<br>(9) <sup>a</sup>   | 36.1<br>(47) <sup>a</sup> , (20) <sup>b</sup> |
| $\text{Cl}^+$    | —           | —                         | 27<br>(34) <sup>a,c</sup> , (34) <sup>b</sup> |
| $\text{Cl}_2^0$  | —           | —                         | 5<br>(5.2) <sup>b</sup>                       |
| $\text{SO}_4^0$  | 3           | 0.3<br>(0.1) <sup>a</sup> | 5<br>(4) <sup>a,c</sup> , (4.4) <sup>b</sup>  |
| $\text{HCO}_3^+$ | 4.5         | 0.30                      | 6.2<br>(3.6) <sup>b</sup>                     |
| $\text{CO}_3^0$  | 1           | 88<br>(90) <sup>a</sup>   | 19<br>(14) <sup>a</sup> , (45) <sup>b</sup>   |
| $\text{OH}^+$    | 0.7         | 2.80<br>(2) <sup>a</sup>  | 1.7<br>(1) <sup>a</sup> , (1.8) <sup>b</sup>  |
| <i>Cobalt</i>    |             |                           |   |
| $\text{Co}^{++}$ | 90.8        | 28                        | 47.4<br>(58) <sup>a</sup> , (50) <sup>b</sup> |
| $\text{Cl}^+$    | —           | —                         | 29<br>(30) <sup>a</sup> , (27) <sup>b</sup>   |
| $\text{SO}_4^0$  | 3.4         | 0.20<br>(1) <sup>a</sup>  | 5<br>(5) <sup>a</sup> , (5) <sup>b</sup>      |
| $\text{HCO}_3^+$ | 3.7         | 0.2                       | 6<br>(6) <sup>b</sup>                         |
| $\text{CO}_3^0$  | 1.8         | 69.3<br>(73) <sup>a</sup> | 11<br>(6) <sup>a</sup> , (10.5) <sup>b</sup>  |
| $\text{OH}^+$    | 0.3         | 2.3<br>(7) <sup>a,c</sup> | 1.6<br>(1) <sup>a</sup> , (1.5) <sup>b</sup>  |

<sup>a</sup>Turner *et al* (1981); <sup>b</sup>Mantoura *et al* (1978); <sup>c</sup> given as sum of species of various charges (Mantoura *et al* 1978).

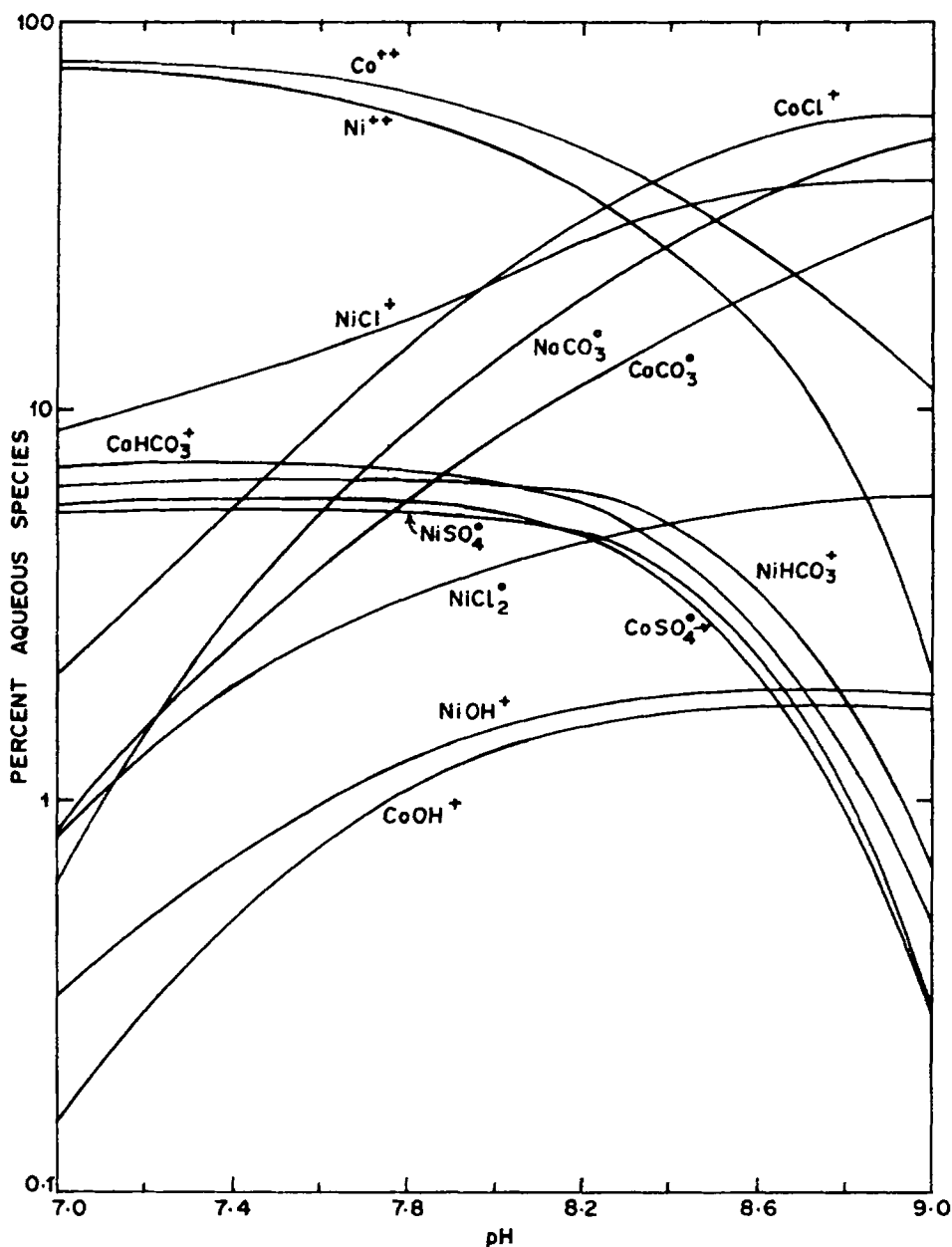


Figure 2. Inorganic complexation of nickel and cobalt in sea water.

complexes are also considered and their contribution is significant (6% at pH 8.2 in sea water).

Extensive computations based on the Long and Angino method (1977) were carried out to obtain graphic diagrams of various mixing ratios of fresh and sea water. To conserve space, only one mixing ratio of 25% sea water and 75% fresh water for both nickel and cobalt is shown in figure 3. As is clear from the figure, on mixing a small

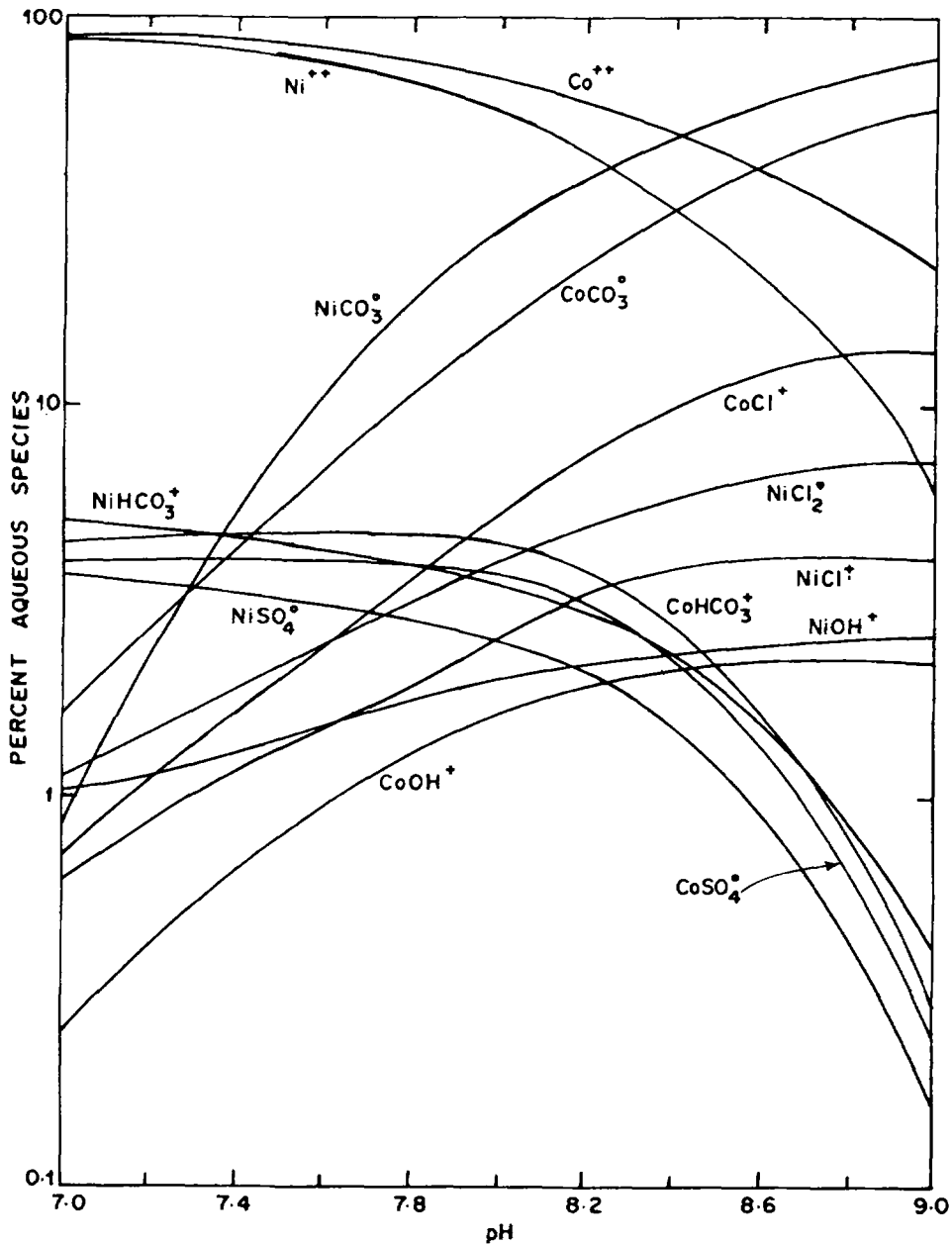


Figure 3. Inorganic complexation of nickel and cobalt in 25% sea water and 75% fresh water.

amount of sea water with fresh water, chloro complexes become significant in both the cases. This condition may be expected at nearshore environs such as deltas or estuaries. Carbonato complexes form more than 50% of the whole at higher pH ( $NiCO_3^0$  60 and  $CoCO_3^0$  50% at pH 9). Chloro complexes contribute 11 and 14% at pH 9 for nickel and cobalt respectively and show poor variation with increasing pH.

As one goes from pure fresh water to pure sea water, a higher order association of chloride complexes would be expected (as in zinc) but such a process does not occur in these metals. In the cases of very high concentrations of fresh water with low amounts of sea water, it is observed that the concentration of ligand controls the speciation pattern and a 5 to 10 per cent addition of sea water is enough for such a change. This type of behaviour may be expected by mixing solutions of high and low ionic strengths.

One important feature regarding nickel is observed on mixing a little fresh water (~ 10%) with sea water. In this solution, the  $\text{NiCl}_2^0$  species is higher than  $\text{NiCl}^+$  but as one progressively uses pure sea water,  $\text{NiCl}^+$  dominates over  $\text{NiCl}_2^0$  and thus the trend is reversed.

As a matter of fact, graphic diagrams for such theoretical computations depend on the selection of stability constants. This is the reason why our values of a few species differ from reported values. Since the values of stability constants used in this work are critically examined by Turner *et al* (1978), it is felt that results of the calculations are reliable. Until experimental results either by ESR or resin exchange techniques are made available, these values could be used. During the computations, various expressions (Mantoura *et al* 1978) for estimating the activity coefficients of metal ions and complexes were attempted. It however, does not make any significant impact on the final results and the conclusion drawn remains the same.

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