

INORGANIC COBALT SPECIES IN SEAWATER

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Summary

Based on polarographic and solubility experiments and the data already published, the distribution of dissolved inorganic cobalt species in seawater was evaluated. The free cobalt ion (hydrated) is the predominant species (about 45%) and CoSO_4° and CoCl^+ are found in approximately equal amounts (about 22%), while the fractions of CoOH^+ , Co(OH)_2° and CoCO_3 are between 1% and 5%.

Résumé

La distribution des espèces inorganiques dissoutes du cobalt dans l'eau de mer est évaluée d'après l'étude des produits de solubilité, des expérimentations faites par polarographie et des constantes de stabilité déjà publiées.

Le cobalt est principalement sous forme d'ion libre (hydraté) (environ 45%); CoSO_4° et CoCl^+ sont en quantités approximativement égales (environ 22%) tandis que la proportion des espèces CoOH^+ , Co(OH)_2° et CoCO_3 varie entre 1% et 5%.

A nuclear power station, during normal operation, releases radioactive cobalt into the aquatic environment. Cobalt accumulates in organisms and is a very toxic element¹. Therefore, the mechanism of the cobalt elimination process from the dissolved forms by precipitation and interaction with suspended matter (organic and inorganic) as well as the uptake into aquatic organisms is of growing interest. The toxicity of heavy metals for marine organisms is correlated with the distribution of their species in seawater². To understand the physico-chemical and biological reactivity of cobalt and its transport through trophic levels of the aquatic ecosystem, the knowledge of its physico-chemical state is of basic importance.

In this work polarographic and precipitation methods were used for cobalt speciation taking into account only the major components of seawater, such as chloride, sulphate, carbonate and hydrogencarbonate. The corresponding constants were experimentally determined at the seawater ionic strength from the shift of the half-wave potential and solubility limits. The value for the carbonato complex was obtained for the first time, while the hydroxo- and sulphato-complex values are in a fairly good agreement with the data already published. The value for the chloro complex at the seawater ionic strength could not be determined directly. Data published for various ionic strengths show great discrepancies. The values obtained in this work at $I=2$ and 3.5 mol dm^{-3} fit well in with the curve β_1 vs. $I^{1/2}$ constructed with the selected values already published³. By extrapolation, the value for the seawater ionic strength was evaluated. A survey of the constants applied is given in Table 1.

Table 1. Equilibrium constants for cobalt(II) complexes with major inorganic anions in seawater, determined in model systems

Homogeneous equilibria	log K	l/mol dm ⁻³	Reference
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	13.75	0.5	3
$\text{Co}^{2+} + \text{H}_2\text{O} = \text{CoOH}^+ + \text{H}^+$	-8.96	0.56	this work
$\text{Co}^{2+} + 2\text{H}_2\text{O} = \text{Co}(\text{OH})_2^0 + 2\text{H}^+$	-17.36	0.56	this work
$\text{Co}^{2+} + \text{CO}_3^{2-} = \text{CoCO}_3^0$	3.15	0.56	this work
$\text{Co}^{2+} + \text{SO}_4^{2-} = \text{CoSO}_4^0$	1.50	0.56	this work
	-0.05	1	3
	-0.14	2	3
	-0.26	3	3
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	-0.11	2	this work
	-0.30	3.5	this work
	-0.009	sea water	extrapolated

The calculated cobalt species distribution in the seawater is presented in Table 2. Concentrations of free inorganic ligands have been taken from three different models^{4,5,6}. It is obvious that the free cobalt ion (hydrated) is the predominant species for all the models examined. Independent polarographic determination, in the artificial seawater, proved that the 2+ is the charge of the predominant species. The other two species CoSO_4^0 and CoCl^+ , are found in approximately equal amounts (about 22%). It was also found that the fraction of the other three complexes considered - CoOH^+ , $\text{Co}(\text{OH})_2^0$ and CoCO_3^0 - are between 1% and 5%.

Table 4. Distribution of dissolved inorganic cobalt(II) species in seawater, calculated using equilibrium constants from Table 1 and three different concentrations of major inorganic ligands (4-6).

Conc. of major inorganic ligands	%Co ²⁺	%CoCl ⁺	%CoSO ₄ ⁰	%CoOH ⁺	%Co(OH) ₂ ⁰	%CoCO ₃ ⁰
(4)	45.1	24.5	21.9	4.9	2.0	1.5
(5)	43.7	23.7	25.3	4.8	1.9	0.7
(6)	49.8	27.6	17.8	5.5	2.2	1.0

	Tot. SO ₄ mol dm ⁻³	Free SO ₄	Tot. and free Cl ⁻ mol dm ⁻³	Tot. CO ₃ ⁼ mol dm ⁻³	Free CO ₃ ⁼
(4)	0.0284	54%	0.5543	0.000296	9.0%
(5)	0.02909	62.9%	0.5543	0.00011	10.2%
(6)	0.02906	39%	0.5652	0.000171	8.0%

References

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4. Garrels, R.M. and Thompson, M.E. (1962), Amer. J. Sci. 260, 57.
5. Hanor, J.S. (1969), Geochim. Cosmochim. Acta 33, 894.
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"Inorganic cobalt species in seawater"

Paper presented by M. Branica (Yugoslavia)

Discussion

- P. Valenta: a) Is the CoCl^+ the only cobalt chloro complex?
 b) The interpretation of the stability constant for hydrated ion.
 c) Applicability of the $E_{1/2}$ -shift method for irreversible waves.
- M. Branica: a) According to our polarographic results obtained in the solution of different chloride concentrations up to 3 mol dm^{-3} the complexation of cobalt(II) with chloro ligands is weak and the only monochloro cobalt complex is noticed.
 b) The solubility of cobalt hydroxide and the corresponding hydrolysis constant of cobalt(II) were obtained from the precipitation experiments from different pH solutions and composite electrolyte of NaClO_4 and NaCl with constant $I=0.56 \text{ mol dm}^{-3}$.
 c) The $E_{1/2}$ -shift method for determination of stability constants is applicable for irreversible polarographic waves with constant electrode kinetic parameters (k_s and α) in the investigated concentration range of the complexing ligand

as it is fulfilled for Co(II) in the seawater conditions. More details are elaborated in the paper: B. Čosović, D. Degobbis, H. Bilinski, M. Branica, Inorganic Cobalt Species in Seawater, *Geochim. Cosmochim. Acta*, in press.

G. Cauwet: What about the organic forms?

M. Branica: The role of organic cobalt species in seawater can not be discerned by the speciation of inorganic cobalt here presented. The biogeochemical reactivity of cobalt in seawater based on the residence time (780 yrs) is lower than that of Fe and Mn (30 and 53 yrs, respectively) but higher than that of Cu, Zn, and Cd. The latter metals with higher residence times are removed from the water column considerably more slowly, because of their pronounced interaction with organic matter and biological components. From the comparison of residence time of different metals it seems very likely that the reactivity of cobalt has an important role for very fast removal of dissolved cobalt(II) from the ocean water column. Because of heavy metal competition for organic ligands the relatively low Co concentration in seawater has to be taken in account too.

Lj. Musani: The organic complexation of cobalt is considered only in rather polluted areas with substances having high stability constants with cobalt (order of magnitude of Co-EDTA complex). At the EDTA concentration of 10^{-7} M cobalt in seawater forms EDTA-complexes showing a slow rate reaction.

H.W. Nürnberg: The exchange of the water dipoles from the primary hydration shell of hydrated Co(II) is indeed a process with a rather moderate rate. In 1963 we have determined the rate constant by advanced voltammetry (High level Faradaic Rectification Polarography): The heterogeneous k-value is about 10^6 cms^{-1} . This corresponds to a homogeneous rate constant of -0.1 s^{-1} for water exchange from the hydration shell Co(II).

A. Ballester: Can you describe the basic mechanisms of Co precipitation?

M. Branica: Our precipitation measurements were done at equilibrium conditions, and $\text{Co(OH)}_2 \text{ (s)}$ was assumed to be a solid phase. Additional research using kinetic measurements and applying a more sophisticated instrumental analysis could yield more detailed knowledge for elucidation of governing chemical mechanisms.

