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The Stability Constants of Nickel(II) Complexes with Chloride, Thiocyanate, Sulfate, Thiosulfate, and Oxalate Ions, as Determined by a Solvent Extraction Method

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Synopsis. The stability constants of nickel(II) complexes in 1 mol dm^{-3} sodium perchlorate media were determined at 25 °C by means of a solvent extraction method. The values thus obtained for log β_1 and log β_2 are: 0.0 and no second complex (Cl^-), 1.1 and 1.6 (SCN^-), 1.0 and 1.4 (SO_4^{2-}), 0.9 and 1.3 ($S_2O_3^{2-}$), and 3.7 and 6.6 ($C_2O_4^{2-}$), respectively.

Although there have been several reports on the stability constants of nickel(II) complexes with various common anions, most of them have been studied in dilute electrolyte solutions.[1,2] In order to obtain these constants at higher electrolyte concentrations, which are often necessary for various analytical purposes, experiments were made in 1 mol dm^{-3} sodium perchlorate media at 25 °C by means of a solvent extraction method.

Experimental

All the procedures, based on the synergic metal chelate extraction method,[3] were carried out at 25±0.3 °C in a way similar to that described in previous reports.[4,5] The aqueous phase was a 1 mol dm^{-3} $Na(ClO_4)$ medium containing about 10^{-4} mol dm^{-3} of nickel(II), 1×10^{-2} mol dm^{-3} of a sulfanilate buffer, and a certain amount of the ligand anion. This amount of buffer kept the hydrogen-ion concentration about 10^{-3} mol dm^{-3} and has a negligible effect on the extraction. The organic phase was carbon tetrachloride containing 5×10^{-2} mol dm^{-3} of thenoyltrifluoroacetone (TTA) and 3×10^{-2} mol dm^{-3} of trioctylphosphine oxide (TOPO). A 5 ml portion of each solution was placed in a stoppered glass tube and agitated mechanically until the distribution equilibrium was reached; then the whole was centrifuged. The optical absorbance of this organic phase was measured at 410 nm by means of a spectrophotometer. The hydrogen-ion concentration was measured by means of a potentiometer. A correction was made for the dissociation of the hydrogen oxalate ion by using a value of 3.54 for pK_{a2} in 1 mol dm^{-3} perchlorate media at 25 °C.[6]

Statistical

The stability constants of complexes with a L_l^- ligand are:

$$\beta_n = [NiL^{2-nl}][Ni^{2+}]^{-1}[L^{l-}]^{-n} \qquad (1)$$

The equilibrium constant for the extraction of the Ni^{2+} ion with a chelating extractant, HA, can be written as:

$$Kex = [NiA_2]_{org}[H^+]^2[Ni^{2+}]^{-1}[HA]_{org}^{-2} \qquad (2)$$

where "org" denotes a species in the organic phase and where the lack of any subscript denotes a species in the aqueous phase. Even when a synergist which forms adduct chelates with the NiA_2 complex is present, its term can be omitted as long as its concentration is kept constant.[3] When nickel(II) is present in the organic phase as the NiA_2 species and in the aqueous phase as the Ni^{2+}, NiL^{2-l}, and NiL_2^{2-2l} species, the distribution ratio can be written as:

$$D = [NiA_2]_{org}/([Ni^{2+}]+[NiL^{2-l}]+[NiL_2^{2-2l}]) \qquad (3)$$

When the distribution ratio in the absence of L^{l-} is denoted by D_0, the following equation can be obtained from Eqs. (1) to (3):

$$D[H^+]^2[HA]_{org}^{-2}Kex^{-1} = (1+\beta_1[L^{l-}]+\beta_2[L^{l-}]^2)^{-1} \qquad (4)$$

When the results are plotted in the form of log $D[H^+]^2[HA]_{org}^{-2}Kex^{-1}$ vs. log $[L^{l-}]$, the stability constants can be determined by a curve-fitting method.[6]

Results and Discussion

In the absence of TOPO, the extraction of nickel(II) with TTA in carbon tetrachloride was poor and the

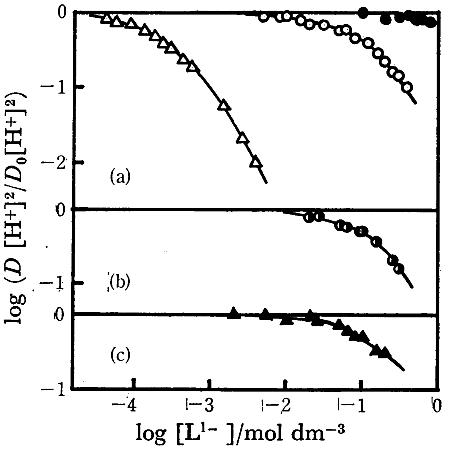

Fig. 1. Decrease in the extraction by complex formation. The ligands are as follows. (a) $C_2O_4^{2-}$ (△), SCN^- (○), and Cl^- (●), (b) SO_4^{2-} (◑), and (c) $S_2O_3^{2-}$ (▲). The curves were obtained by introducing the constants in Table 1 into Eq. (4).

Table 1. Stability constants of nickel(II) and cobalt(II) complexes in 1 mol dm^{-3} sodium perchlorate solution at 25 °C

Ligand	Ni(II)[a]		Co(II)[b]	
	log β_1	log β_2	log β_1	log β_2
Cl^-	0.0	—	−0.5	—
SCN^-	1.1	1.6	1.00	1.32
SO_4^{2-}	1.0	1.4	0.74	1.48
$S_2O_3^{2-}$	0.9	1.3	0.84	0.88
$C_2O_4^{2-}$	3.7	6.6	3.33	6.20

a) Present work. b) From Refs. 4 and 5.

results were not reproducible. In its presence, however, reasonable results, which can be represented by Eq. (4), were obtained in the range of $10^{-2} < D < 10$. Figure 1 gives the experimental data. The stability constants obtained are listed in Table 1, together with those of the cobalt(II) complexes previously reported.[4,5] It may be seen from the table that the stability constants of the nickel(II) complexes are, in general, a little higher than those of the corresponding cobalt(II) complexes, as is to be expected from the natural order of stability, although the difference is not large.

The values of the stability constants for these complexes in the literature[1,2] are rather scattered, and, since many of them were obtained at low electrolyte concentrations, a direct comparison with the present results is not possible. However, the previous values for the β_1 of the chloride complex in 1.5 to 2 mol dm^{-3} perchlorate media are somewhat lower than the present values, while those for the β_1 of thiocyanate complexes in 1 to 2 mol dm^{-3} perchlorate media, about $10^{1.2}$, agree well with the present value.

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