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FORMATION OF MIXED METAL COMPLEX IN THE EXTRACTION OF COBALT AND NICKEL WITH CAPRIC ACID IN BENZENE

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A mixed metal complex was found in the extraction of cobalt and nickel with capric acid (HR) in benzene at 25°C and ionic strength of about 0.1 M in $NaClO_4$. The extraction equilibrium is formulated as: $Co^{2+} + Ni^{2+} + 4\ (HR)_{2,o} \rightleftharpoons (CoNiR_4 4HR)_o + 4\ H^+$, and $\log K_{mix} = -19.1 \pm 0.1$.

In our previous papers[1,2] on the extraction of cobalt(II) and nickel ions with capric acid (n-decanoic acid, abbreviated as HR) in benzene, the formation of dimeric and monomeric metal caprates in the organic phase has been reported. The extraction of a metal M is generally described as follows:

$$j\ M^{2+} + \frac{j(2+x)}{2}\ (HR)_{2,o} \rightleftharpoons (MR_2xHR)_{j,o} + 2j\ H^+ \tag{1}$$

$$K_{jx} = [(MR_2xHR)_j]_o\ [H^+]^{2j}\ [M^{2+}]^{-j}\ [(HR)_2]_o^{-\frac{j(2+x)}{2}} \tag{2}$$

where $[H^+]$ is the hydrogen ion concentration and the subscript o is used to indicate the organic phase. In the case of cobalt and nickel x is 4 for j = 1, while x is 2 for j = 2: $MR_2 4HR$ and $(MR_2 2HR)_2$ are formed in the organic phase.

Extraction of metal carboxylates was applied to the elimination of cobalt involved as impurity in a nickel salt of reagent grade. A preliminary radiometric experiment using ^{60}Co as a tracer was carried out on a solution containing 0.20 M nickel sulfate and 10^{-4} M cobalt, 1.80 M capric acid in benzene being utilized as an extractant. This experiment revealed that the extractability of cobalt caprate was higher than predicted from the above extraction constants K_{jx} for cobalt. This phenomenon could be well explained by formation of a mixed metal complex (cobalt nickel caprate) in the organic phase.

Suppose the following reaction in system involving both cobalt and nickel:

$$p\ Co^{2+} + q\ Ni^{2+} + (p+q+\tfrac{x}{2})\ (HR)_{2,o} \rightleftharpoons (Co_pNi_qR_{2(p+q)}xHR)_o + 2(p+q)\ H^+ \quad (3)$$

$$K_{mix} = [Co_pNi_qR_{2(p+q)}xHR]_o[H^+]^{2(p+q)}[Co^{2+}]^{-p}[Ni^{2+}]^{-q}[(HR)_2]_o^{-(p+q+\frac{x}{2})} \quad (4)$$

An excess metal concentration in the benzene phase ($C'_{M,o}$) is defined as:

$$C'_{M,o} = C_{M,o} - [MR_24HR]_o - 2\ [(MR_22HR)_2]_o \quad (5)$$

$$r = C'_{Ni,o}\ /\ C'_{Co,o} = q\ /\ p \quad (6)$$

where $C_{M,o}$ refers to the total concentration of a metal M.

For the calculation of $C'_{M,o}$ the extraction constants K_{14} and K_{22} of both metals were newly determined by using 0.01000 M $HClO_4$ aqueous solution as a pH standard (ph $\equiv -\log\ [H^+] = 2.000$), because 0.05 M potassium hydrogen phthalate solution was employed in the previous works[1,2] ($pa_H = 4.008$ at 25°C [3]).
The results are given below:

$$\log K_{14} = -11.21 \pm 0.05 \text{ and } \log K_{22} = -19.82 \pm 0.05 \text{ for cobalt}$$

$$\log K_{14} = -11.27 \pm 0.05 \text{ and } \log K_{22} = -19.17 \pm 0.1 \text{ for nickel} \quad (7)$$

All experiments were carried out at 25 ± 0.2°C and ionic strength of about 0.1 M in $NaClO_4$. Analytical concentrations of both metals were differentially determined by the compleximetric titration.[4]

Experimental values of r ranged from 0.8 to 1.2. In view of the inaccuracy of $C'_{M,o}$, which is very sensitive to a variation of K_{jx}, the value of r may be considered to be unity.
When r = 1, the following expression is derived from Equation (4):

$$\log C'_{Ni,o} = p(\log[Co^{2+}] + \log[Ni^{2+}] + 4\ ph) + (2p+\tfrac{x}{2})\ \log[(HR)_2]_o + \log p + \log K_{mix} \quad (8)$$

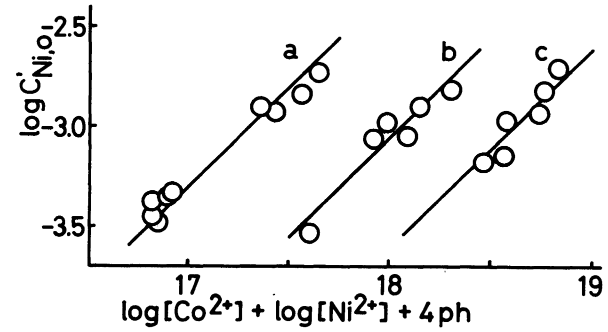

Fig. 1 Determination of the number of metals incorporated in a mixed complex. Capric acid concentrations: a — 1.00 M, b — 0.700 M, c — 0.500 M.

Fig. 1 illustrates a linear dependence of log $C'_{Ni,o}$ on (log$[Co^{2+}]$ + log$[Ni^{2+}]$ + 4 ph) at a fixed concentration of extractant. The slope of unity indicates that p = q = 1. Then from Equation (8) we have the following expression:

$$\log C'_{Ni,o} - (\log[Co^{2+}] + \log[Ni^{2+}] + 4\ ph) = (2+\frac{x}{2}) \log[(HR)_2]_o + \log K_{mix} \qquad (9)$$

As seen from Fig. 2, the plot of the values for the left-hand side of Equation (9) against logarithmic concentrations of capric acid falls close to a straight line with a slope of 4, that is x = 4. Thus it is concluded that the coextracted species is $CoNiR_4 4HR$ with the corresponding extraction constant: log K_{mix} = -19.1 ± 0.1.

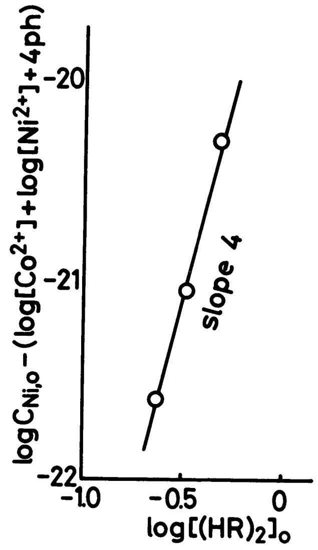

Fig. 2 Determination of the number of capric acid coordinated to the central metal ions. The slope is $2 + \frac{x}{2}$.

This conclusion may be quite reasonable, since both metals form dimeric caprates of the type $M_2R_4 4HR$ and the value of log K_{mix} is comparable with the relevant extraction constants K_{22} for dimeric cobalt and nickel caprates.

Electronic spectra for the coextracted species are quite similar to those composed of each spectrum for dimeric caprate, that is, the additivity of spectra holds for the mixture of cobalt and nickel caprates. This fact implies that the octahedral environments about both central metal ions in the mixed metal complex resemble closely those in their respective dimeric caprates.

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