Studies on the Mixed Complexes of Ni(II)-Oxinate with Pyridine, α-, β- & γ-Picolines, Quinoline & Isoquinoline & Their Analytical Applications

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The formation of mixed complexes of nickel(II) with oxine and some neutral nitrogen donors such as pyridine, α-, β- and γ-picolines, quinoline and isoquinoline has been studied using solvent extraction technique. The composition of the extracting species is found to be $Ni(Ox)_2B_2$ where B is the nitrogen donor. The equilibrium constants of the mixed complexes have been determined. The order of effectiveness of these donors both in forming mixed complexes and as synergists is found to be : γ-picoline > β-picoline > pyridine and isoquinoline > quinoline. The nickel(II)-oxine-isoquinoline system exhibits λ_{max} at 410 nm with a molar extinction coefficient of 7900 ± 100 and obeys Beer's law up to 12 µg Ni(II)/ml. In the application of this method for the determination of nickel in various steel samples, only copper and cobalt are found to interfere. Methods for the elimination of interference of some other cations are proposed.

ZOLOTOV *et al.*[1] studied the spectral characteristics of the ternary complex, nickel (II)-oxine-pyridine in benzene. However, the extraction characteristics of such mixed complexes have not been investigated so far. The results on the extraction of the mixed complexes of Ni(II)-oxine complex with pyridine and quinoline bases and their analytical applications are presented in this paper.

Materials and Methods

A Beckman DU-2 spectrophotometer and a Philips *p*H meter were used.

Nickel(II) sulphate solution was prepared by dissolving $NiSO_4 \cdot 7H_2O$ (AR, BDH) in doubly distilled water containing a few drops of dilute H_2SO_4 to prevent hydrolysis and standardized by dimethylglyoximate method.

A stock solution ($0.2M$) of 8-hydroxyquinoline (AR, BDH) was prepared in dilute ($\sim 0.1N$) sulphuric acid and standardized by bromometric method.

Pyridine (AR, BDH), α-picoline (E. Merck), β-picoline (E. Merck), γ-picoline (E. Merck), quinoline (WB, England) and isoquinoline (Pure, Fluka) and all solvents (BDH) used were freshly distilled before use. Other chemicals used were of AR grade.

General extraction procedure — Nickel(II) solution (5 ml) containing up to about 200 µg of the metal and oxine solution (2 ml, $0.1M$) were mixed and *p*H adjusted to 7. The volume was made up to 20 ml and equilibrated for 2 min with a solution of the base (20 ml, 10%) in benzene (30% in the case of quinoline). The organic phase was separated and dried over anhydrous sodium sulphate. The absorbance of the organic phase was measured at 410 nm against reagent blank.

Results

Pyridine, picolines and isoquinoline systems show quantitative extraction as well as maximum colour in the *p*H range 5-10 while *p*H 6-8 is the range for the quinoline system. *p*H 7 is chosen for further studies.

The mixed complexes are extractable into most of the common solvents like benzene, chloroform, *n*-butanol, isobutyl methyl ketone, nitrobenzene, 1,2-dichloroethane, carbon tetrachloride, etc. However, benzene extract exhibits the maximum absorbance.

Just a 3-fold excess of oxine and about 500-fold (12000-fold for quinoline and 50% for α-picoline) excess of base are sufficient to secure maximum colour and extraction in all the systems.

A single one-minute equilibration is sufficient for maximum recovery of nickel as well as for full development of colour in the organic phase. The colour of the extract is stable for more than 24 hr. The absorption spectra of all the systems show maximum absorbance at 410 nm. Beer's law is obeyed up to about 10 µg of Ni(II)/ml in all the systems.

Of all the systems, isoquinoline system is found to be the most sensitive in view of its high molar absorptivity (7900 ± 100 litre mole^{-1} cm^{-1}) with a sensitivity[2] of 0.0074 µg of nickel per cm^2. This colour reaction has been developed into a rapid and sensitive spectrophotometric method for the determination of nickel.

Composition of the extracting species — The composition of the extracting species in all the systems is found to be 1:2:2 (nickel: oxine: base). Oxine number is determined by the slope analysis of curves obtained from $\log q$ vs $\log[HO_x]_{total}$ plots and by Job's method of continuous variations

keeping a constant excess of base. The quantity q is calculated by determining the amount of nickel present in the aqueous phase, after equilibration, by adding excess of oxine and the corresponding base and equilibrating with benzene (20 ml) at pH 7 and measuring the absorbance of the extract at 410 nm and computing the amount of nickel from the corresponding Beer's law curve.

Base number could not be determined by studying the variation of q with the variation of [base], since, irrespective of the presence of a base, a 3-fold excess of oxine is sufficient to effect quantitative extraction of Ni(II) as a colourless 1:2 complex[3]. So we have chosen to study the change in absorbance of the extract with the base variation in the presence of 3-fold excess of oxine, which is not sufficient for the formation of coloured Ni(II)-oxine binary complex[3]. The formation and extraction of the mixed complex is given by

$$[Ni(Ox)_2] + n[B] \rightleftharpoons [Ni(Ox)_2B_n]_0$$

$$K = \frac{[Ni(Ox)_2B_n]_0}{[Ni(Ox)_2][B]^n} \qquad \ldots(1)$$
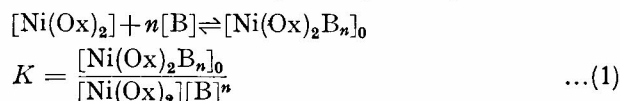
where K is the adduct constant, and o denotes the organic phase. Further

$$[C_{Ni}]_o = [Ni(Ox)_2B_n]_o + [Ni(Ox)_2]_o \qquad \ldots(2)$$

where $[C_{Ni}]_o$ is the total nickel concentration in the organic phase. Since there is quantitative extraction under the experimental conditions, $[C_{Ni}]_o$ is the same as the concentration of nickel initially taken. $[Ni(Ox)_2B_n]_o$, the concentration of the mixed complex in the organic phase, is obtained from the absorbance of the extract. $[Ni(Ox)_2]_o$ is the difference between these two, i.e. $([C_{Ni}] - [Ni(Ox)_2B_n]_o)$.

Substituting these values in Eq. (1), taking logarithms and rearranging, we get

$$\log K + n \log[B] = \log\left[\frac{[Ni(Ox)_2B_n]_o}{[C_{Ni}]_o - [Ni(Ox)_2B_n]_o}\right] \qquad \ldots(3)$$

According to Eq. (3) the plot of

$$\log\left[\frac{[Ni(Ox)_2B_n]_o}{[C_{Ni}]_o - [Ni(Ox)_2B_n]_o}\right] \text{ vs } \log[B]$$

should be linear of slope n which is the ratio of base to nickel(II) in the extracting species. Fig. 1 shows such a plot for the isoquinoline system. The ionic strength is maintained constant at $0.5M$ with Na_2SO_4 in these experiments as well as in those for the determination of stability constants. Sulphate is preferred to perchlorate or nitrate or chloride because it is without any influence on the formation and extraction of nickel(II)-oxine complex while the other anions form mixed complexes[4,5].

Stability of the mixed complexes — While adduct constants, given in Table 1, can be calculated from Eq. (3), the overall equilibrium constant is obtained from the expression derived as follows:

$$[Ni^{2+}]_{aq} + 2[Ox^-]_{aq} + 2[B]_{aq} \rightleftharpoons [Ni(Ox)_2B_2]_{aq}$$
$$\Updownarrow$$
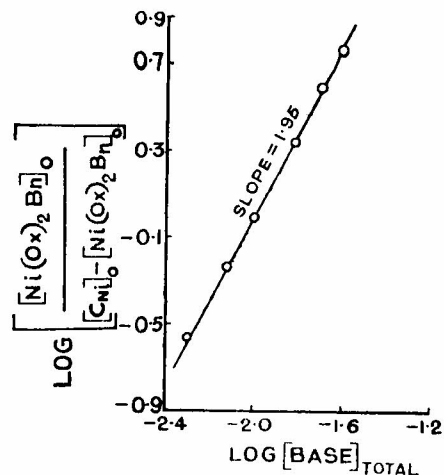$$[Ni(Ox)_2B_2]_o \qquad \ldots(4)$$
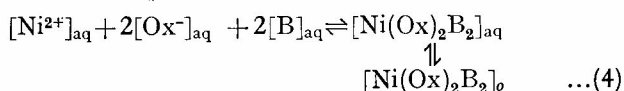
is given by Eq. (5)

Fig. 1 — Determination of base number [Aqueous phase: Ni(II) = $1.0 \times 10^{-4}M$; oxine = $3.0 \times 10^{-4}M$; pH = 7.0; total volume = 20 ml; total ionic strength = $0.5M$. Organic phase: 20 ml of different amounts of isoquinoline in benzene]

TABLE 1 — STABILITY OF THE MIXED COMPLEXES

System	ϵ (± 100) litre (mole^{-1} cm^{-1})	Adduct constant	$\log \beta_{2,2}$ (at $29°$)	[Base] req. for conversion of 50% Ni(II) into mixed complex (M)†
Ni(II)-Oxine*	5,500	—	20.32 ($\log \beta_{2,o}$)	—
Ni(II)-Ox-pyridine	7,000	4.66	23.57	0.019
Ni(II)-Ox-β-picoline	7,100	5.86	24.97	0.011
Ni(II)-Ox-γ-picoline	7,400	5.91	26.27	0.0105
Ni(II)-Ox-quinoline	6,800	4.65	23.95	0.525
Ni(II)-Ox-isoquinoline	7,900	8.11	28.80	0.010

*Unpublished work.
†Ni(II) = $1.0 \times 10^{-4}M$; [HOx] = $3.0 \times 10^{-4}M$.

$$\beta_{2,2} = \frac{[Ni(Ox)_2B_2]_o}{[Ni^{2+}]_{aq}[Ox^-]_{aq}^2[B]_{aq}^2} \qquad \ldots(5)$$

The distribution of nickel is given by Eq. (6)

$$q = \frac{[Ni(Ox)_2B_2]_0}{[Ni^{2+}] + [NiOx^+] + [Ni(O)x_2]_{aq} + [Ni(Ox)_2B_2]_{aq} + [NiB_i^{2+}]} \qquad \ldots(6)$$

In the presence of excess of base, Ni(II)-oxinate complex is quantitatively converted into $[Ni(Ox)_2B_2]_{aq}$ which, in turn, is quantitatively extracted into benzene under the experimental conditions. Therefore,

$$q = \frac{[Ni(Ox)_2B_2]_o}{[Ni^{2+}]_{aq}} \qquad \ldots(7)$$

From Eqs. (5) and (7),

$$\beta_{2,2} = \frac{q}{[Ox^-]_{aq}^2[B]_{aq}^2}$$

or $\log q = \log \beta_{22} + 2 \log[Ox^-]_{aq} + 2 \log[B]_{aq}$

The equilibrium concentrations of oxine and bases are calculated using Eqs. (8) and (9) respectively, deduced from mass balance equations.

$$[Ox^-]_{aq} = \frac{[HOx]_{total} - 2[Ni(Ox)_2B_2]_o}{\dfrac{[H^+]_{aq}}{K_1} + p\,\dfrac{[H^+]_{aq}}{K_1} + 1 + \dfrac{[H^+]_{aq}^2}{K_1K_2}} \qquad ...(8)$$

where $p = \dfrac{[HOx]_o}{[HOx]_{aq}}$, $K_1 = \dfrac{[H^+]_{aq}[Ox^-]_{aq}}{[HOx]_{aq}}$ and

$K_2 = \dfrac{[HOx]_{aq}[H^+]_{aq}}{[H_2Ox^+]_{aq}}$, the values of which are taken from literature[6].

$$[B]_{aq} = \frac{[B]_{total} - 2[Ni(Ox)_2B_2]_o}{1 + p_B + \dfrac{[H^+]}{K_{BH^+}}} \qquad ...(9)$$

where p_B and K_{BH^+} are the partition coefficient and ionization constant of the nitrogen base[7]. The K_{BH^+} values are taken from literature[8,9]. The partition data for pyridine, β-picoline and γ-picoline between water and benzene are determined under experimental conditions and found to be 3·0, 8·0 and 8·3 respectively. The partition coefficients for quinoline and isoquinoline are 110 and 114 respectively[8] between water and benzene. The constants obtained are presented in Table 1.

It is clear from these constants that the effectiveness of the nitrogen bases in forming mixed complexes is in the order: γ-picoline > β-picoline > pyridine and isoquinoline > quinoline. This is supported by the fact that the concentration of the neutral donors required to effect 50% mixed complex formation of nickel (Table 1) is in the order pyridine > β-picoline > γ-picoline and quinoline > isoquinoline.

Though there is no question of synergism under optimum conditions, because, even the binary complex is quantitatively extracted, synergistic enhancement of extraction is observed under non-optimum conditions, for example, at pH values below 6. The effectiveness of these bases as synergists also follows the same order.

Analytical applications — The interference of several foreign anions and cations has been investigated by extracting Ni(II) (117 μg) as Ni(II)-oxine-isoquinoline complex into benzene, in the presence of foreign substances by the recommended procedure. Cr^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mo(VI), Bi^{3+}, Sn^{2+}, V(V), Ag^+, W(VI), do not interfere at 10-fold concentrations. While tartrate, citrate, phosphate, thiocyanate, fluoride do not interfere at 100-fold concentrations, there is no interference even at 1000-fold concentrations from halides, halates, perchlorate, nitrate, sulphate, acetate, phthalate, benzoate, oxalate and pyrophosphate.

Fe^{3+}, Al^{3+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} interfere seriously. While 50 mg of pyrophosphate masks Fe^{3+}, Pb^{2+}, Zn^{2+}, UO_2^{2+} up

TABLE 2 — ESTIMATION OF NICKEL* IN STEEL AS Ni(II)-OXINE-ISOQUINOLINE COMPLEX

Sample	Nickel (%)		Relative mean deviation %
	DMG method	Present method†	
Chromium steel (Cr-Ni)	1·67	1·68	0·26
BCS No. 225/1 steel (Ni-Cr-Mo-Mn)	1·54	1·54	0·28
18/8 Stainless steel (Cr-Ni)	8·33	8·34	0·05

*Average of six determinations.
†Standard deviation $5·8 \times 10^{-3}$.

to 0·15, 5, 1 and 2·5 mg respectively, the presence of 3 mg of Mn^{2+}, 0·5 mg of Al^{3+}, 1·5 mg of Cd^{2+} can be tolerated in the presence of 30 mg of hydroxylamine hydrochloride, 15 mg of fluoride and 100 mg of oxalic acid respectively. However, Co^{2+} and Cu^{2+} could not be masked by any of the general masking agents.

This method has been used to determine the amount of nickel present in various steel samples. The steels are dissolved[10] and the amount of nickel is determined by the dimethylglyoximate method[11] and the present method. The results are presented in Table 2.

This method compares favourably with other known methods for the determination of nickel and is more sensitive than the one based on the extraction of nickel-oxinate binary complex.

Acknowledgement

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