NOTES

A Spectrophotometric Study of the Metal Chelates of Resacetophenone Oxime. III. Nickel Chelate

By K. S. Bhatki,[*] A. T. Rane and M. B. Kabadi[**]

(Received July, 16, 1963)

The first two parts of the study of resacetophenone oxime (RAPOX) chelates of copper and iron were published in the Proceedings of the Symposium on the Chemistry of Coordination Compounds, Agra, February, 1959. This paper is an extension of the study of RAPOX chelates of the nickel system.

Experimental

The Preparation and Standardisation of the Reagent Solutions.—*Nickel Solution.*—The solution of nickel sulphate was prepared using Merck's G. R. quality reagent. It was standardised using RAPOX.1) The solution was found to be 7.675×10^{-2} M. Dilute solutions were prepared from the standard solution.

RAPOX.—RAPOX (resacetophenone oxime) was prepared and crystallised in a way which has been described previously.2) The solutions of the required strength were prepared in freshly-distilled cyclohexanone using the recrystallised reagent.

Cyclohexanone.—Cyclohexanone of a B. D. H. technical quality was treated as described by Vogel3) and distilled. A fraction distilling between 153°C and 156°C was collected and stored in amber-coloured glass-stoppered bottles.

The other reagents, such as glacial acetic acid, potassium dihydrogen phosphate, and sodium hydroxide, etc. were of either Merck's (G. R.) or B. D. H. (AnalaR) quality.

Besides cyclohexanone, the other organic solvents were used in the solubility study4) of nickel RAPOXimate. They were chemically-pure reagents supplied by Eastman Organic Chemicals & Co.

Nickel RAPOXimate.—A measured volume of nickel solution was treated with a solution of sodium carbonate to neutralise the mineral acid present. The slight turbidity that developed was eliminated by adding dilute acetic acid. The pH of the resulting solution adjusted to a pH a little higher than 6.2, the required optimum pH for complete precipitation,2) using sodium acetate. The nickel RAPOXimate was then precipiated by the dropwise addition of a two per cent alcoholic solution of RAPOX. After the precipitate had been digested for some time on a hot water bath, it was filtered using a sintered glass crucible with a porocity of 4 (2G4). It was then washed thoroughly free from impurities with hot distilled water. The precipitate was first dried in a vacuum desiccator to a constant weight. Thereafter the precipitate was dried in an air oven at 110°C. The weight of the precitate even after this treatment was the same, indicating the absence of water molecules in the complex in the solid state. It was preserved over fused calcium chloride in a desiccator.

A weighed quantity of the dried complex was treated in a silica crucible, first with nitric acid and then with perchloric acid. After the organic matter had been completely decomposed, the residue was treated in order to estimate the nickel volumetrically.5) The nitrogen in the complex was also estimated by Kjeldahl's method.6) The nickel and nitrogen contents were found to agree with the theory that the composition of the complex is $Ni(C_8H_8O_3N)_2$

The Spectral Study of Nickel RAPOXimate in Cyclohexanone.—A weighed quantity of nickel RAPOXimate was dissolved, and the solution made up to a known volume using freshly distilled cyclohexanone. The spectral examination of the resulting solution was first accomplished on a Beckman DU spectrophotometer, using cyclohexanone as a blank liquid. The detailed study was then carried out using a Lumetron photoelectric colorimeter, model 402-E. The data obtained from these experiments at different wavelengths are given in Fig. 1.

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[*] Member, Chemistry Division, Atomic Energy Establishment Trombay, Government of India, Bombay.

[**] Present address: Maharshi Dayanand College, Bombay-12.

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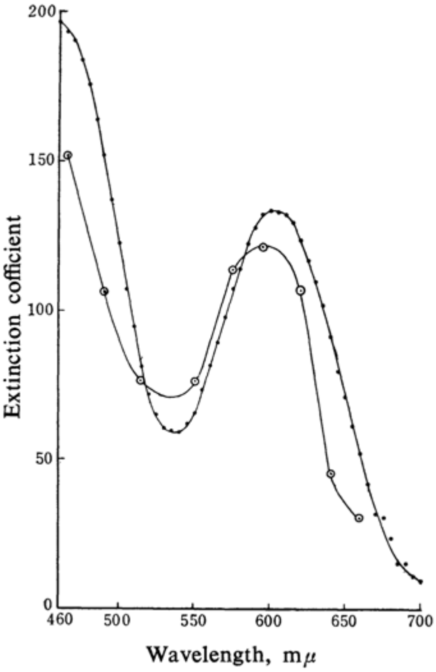

Fig. 1. Spectrum of nickel RAPOXimate in cyclohexanone in the visible region.
- • Beckman spectrophotometer DU
- ⊙ Lumetron colorimeter-402E

A Standard Curve for Nickel.—Since the point of maximum absorption using the Lumetron was observed at 595 M (monochromatric filter), the obedience of Beer's law by the system was checked using the same filter. Several solutions of the complex in cyclohexanone, possessing different concentrations, were subjected to the Lumetron study. The results are recorded in Fig. 2. It is observed under these conditions that the smallest amount of nickel that can be determined is six parts per million. The molar extinction coefficient was found to be $\varepsilon_{595}=132.5$.

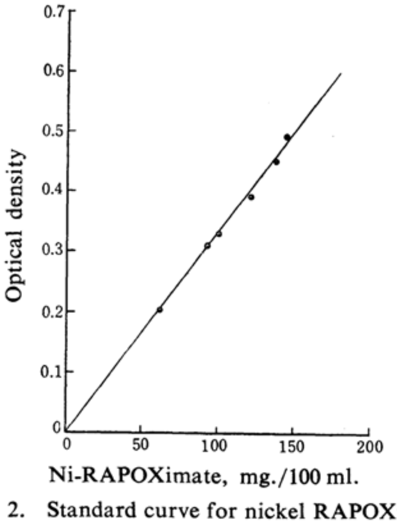

Fig. 2. Standard curve for nickel RAPOXimate in cyclohexanone using 595 M filter.

The Choice of the Solvent for the Extraction Study.—In order to extract nickel from an aqueous solution, it was necessary to choose a suitable water-immiscible solvent. A precise solubility study[4] of nickel RAPOXimate in a few typical water-immiscible solvents was, therefore, undertaken. The different solvents were benzene, nitrobenzene, chloroform, carbon tetrachloride, diisopropyl ether, *n*-butyl ether, amyl acetate, ethyl methyl ketone, methyl isobutyl ketone, diisobutyl ketone and cyclohexanone. In these experiments, the important observation was made that the same amount of nickel RAPOXimate present gave the same optical density, irrespective of the solvent employed, the monochromatic filter being also the same (595 M). Consequently, the standard curve for cyclohexanone can be used as a standard curve for the other solvents also. This observation establishes that the behaviour of nickel RAPOXimate in all the solvents is similar and shows neither association, dissociation nor any complex formation with the solvent itself if no such phenomenon existed in cyclohexanone. It can also be inferred from these findings that in all these solvents the molecular condition of the complex is the same.

Experiments were carried out at a temperature of 30±1°C. From these,[4] it was evident that the solubility of the complex in cyclohexanone was the maximum, 1.710 g. of nickel RAPOXimate per 100 ml. of the solution.

The Partition Study of Nickel RAPOXimate at Various pH Values.—A known and constant volume of the standard nickel solution was pipetted out into several glass-stoppered pyrex centrifuge

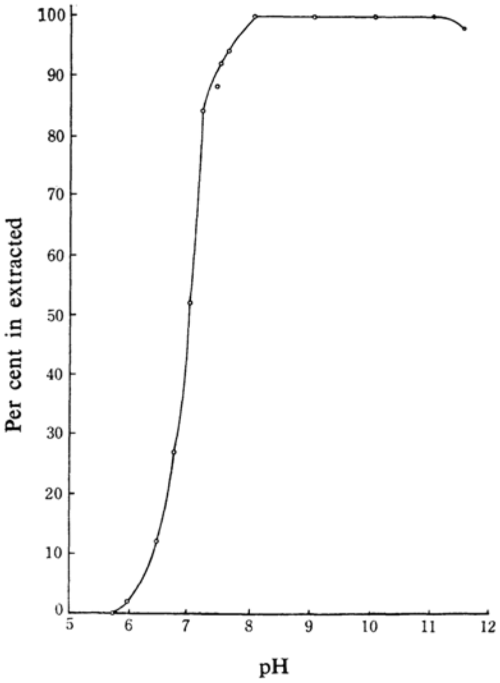

Fig. 3. Extraction of nickel at various pH using RAPOX in cyclohexanone.

tubes. To each of this was added a requisite amount of the buffer solution to fix the pH and then an equal volume of cyclohexanone containing RAPOX. For the sake of maintaining uniformity in the experiment, it was decided to take five times the amount of RAPOX required for the formation of 1 : 2 complex. The tubes were then shaken vigorously on a shaking machine for about eight hours. The phases were separated by centrifuging, and the optical density of the upper organic layer was noted using Lumetron 402-E and 595 M filter. The readings are shown in Fig. 3.

Composition of Nickel RAPOXimate.—The composition of the nickel complex of RAPOX was determined with the help of (i) Job's method7) of continuous variation as extended to a two-phase system by Irving and Pierce8) and (ii) the slope ratio method9,10) modified similarly. These methods, which are generally applicable in case of complexes soluble in an aqueous medium or in an organic medium miscible with water, were employed because they could be so utilised in the present case with the same degree of accuracy. Moreover, the authors experienced no difficulty in extending the slope ratio method to a two-phase system.11)

(*i*) *Job's Method.*—In this method x ml. of nickel sulphate solution (7.675×10^{-3} M) were mixed with a fixed volume of the buffer solution and diluted to 25 ml. ($10-x$) ml. of the RAPOX solution of the same molarity in cyclohexanone diluted to 25 ml. was added to the former aqueous solution, and the mixture was shaken vigorously for a few minutes. The upper layer was then separated carefully after centrifuging and examined by Lumetron using a 595 M filter. The results are surveyed in Fig. 4.

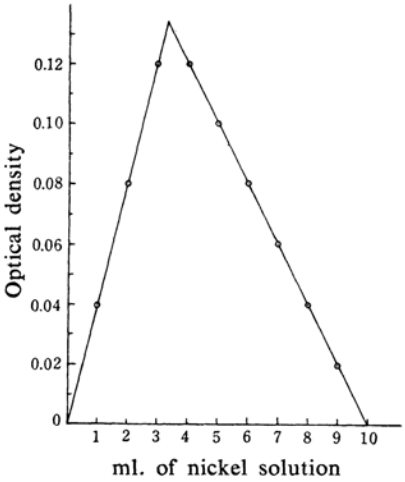

Fig. 4. Job's method in a two phase system.

(*ii*) *The Slope Ratio Method.*—For this purpose two sets of experiments had to be performed. In one, the volume of the nickel solution was kept constant, while that of the reagent was varied. In the other set the volume of the reagent in cyclohexanone was kept constant, whereas that of metal solution was varied. The molarity of the nickel solution and RAPOX in cyclohexanone was the same, namely, 9.225×10^{-3} M.

In the actual experiment different volumes of the standard nickel solution were diluted, each to a fixed volume of 25 ml., after the requisite buffer had been added to bring the pH to 9.0. This mixture was shaken for a few hours with an excess of RAPOX in cyclohexanone, the volume of which was also 25 ml.

In the second set the process was reversed. The volume of the standard RAPOX solution in cyclohexanone was varied and the volume of nickel solution, kept constant. The final volumes of both the aqueous and the organic phase were the same, namely, 25 ml.

The data so collected is surveyed in Fig. 5.

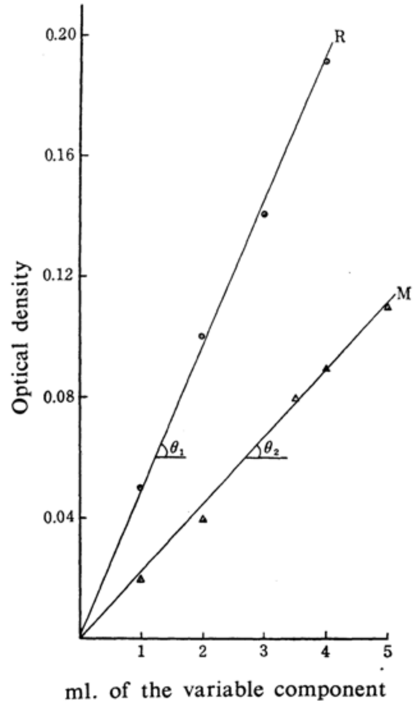

Fig. 5. Slope ratio method in a two phase system.

$\theta_1=67.2°$, $\theta_2=48°$

$$\therefore \frac{\tan\theta_1}{\tan\theta_2}=\frac{2.3789}{1.1106}=2.14$$

⊙ RAPOX in constant excess

△ Ni in constant excess

Back Extraction.—Whenever the extraction of a metal chelate is achieved by an organic solvent, it becomes necessary to recover the metal in a pure form from the organic phase. For this purpose a back extraction study was undertaken.

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8) H. Irving and T. B. Pierce, *J. Chem. Soc.*, **1959**, 2565.

9) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 111 (1944).

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TABLE I. BACK EXTRACTION OF NICKEL FROM ORGANIC PHASE

10 ml. of cyclohexanone containing nickel-RAPOXimate (O. D. = 0.59) is shaken for about 4 hr. with equal volume of aqueous solution at various pH.

Filter, 595 M Temp., 30±1°C Cuvette, 0.5 cm.

Nature of the aqueous solution	O. D. of the org. phase after shaking	Per cent of Ni back extrd.	Remarks
Dilute HCl about 1 N	0.00	100	Even hand shaking for a few minutes was sufficient.
Dilute acetic acid about 2N	0.00	100	RAPOX remained in the org. phase whereas nickel got back extrd. quantitatively as seen by dimethylglyoxime test on aq. phase.
Sodium acetate-HCl buffer pH = 1.09	0.00	100	
Sodium acetate-HCl buffer pH = 2.0	0.00	100	
M/20 K-biphthalate pH = 4.05	0.00	100	
Borate Buffer pH = 8.0	0.59	0.00	Neither the metal nor the reagent got transferred to the aq. phase.
Borax 0.01 M pH = 9.14	0.59	0.00	
Dilute NaOH about 1 N	0.00	100	Reagent too was transferred to the aq. phase with the metal.

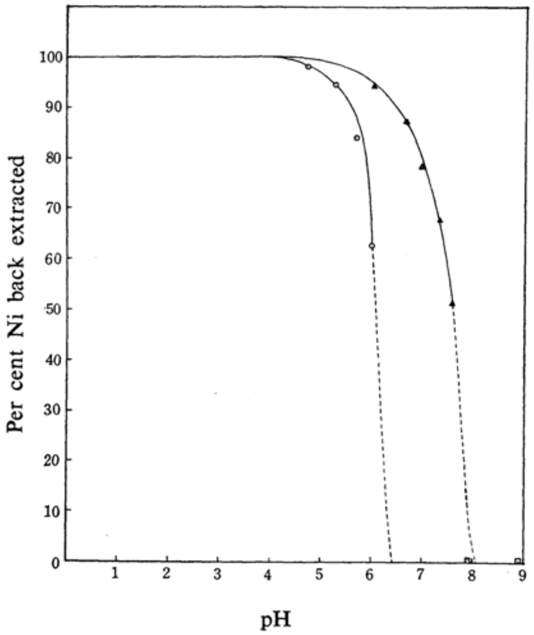

Fig. 6. Back extraction of nickel.
⊙ Phthalate buffer
△ Phosphate buffer
▣ Borate buffer

A cyclohexanone solution of the nickel complex of a known volume and possessing a known optical density was shaken for about four hours with the same volume of an acidic or alkaline solution. The organic layer was centrifuged and its optical density observed. It diminished with an increase in the acidity and also in the alkalinity. The results are given in Table I.

In another experiment a solution of nickel complex was prepared in cyclohexanone saturated with water. A known volume of this was shaken for about eight hours with an equal volume of a buffer solution previously saturated with cyclohexanone. The results are given in Fig. 6.

Discussion

The foregoing study shows a definite complex formation between nickel and RAPOX in the molecular ratio of 1 : 2. An important observation demanding careful consideration is that the extraction of this complex does not appear feasible below pH 6.0 and above 12.00. Under the former condition the formation of the complex is not quantitative, whereas in the latter circumstance the complex seems to decompose, resulting in the transfer of the reagent, along with the nickel ions, to the aqueous phase.

The plot in Fig. 4 is observed to consist of two intersecting straight lines. The point of intersection shows the presence of the complex in solution and corresponds to the concentrations of nickel and RAPOX given by the ratio 3.3 : 6.7 (i. e., 1 : 2). The inference follows that the composition of the complex must be $Ni(C_8H_8O_3N)_2$, in agreement with that composition determined for the complex in the solid state.

The plot in Fig. 4 is observed to be made up of perfectly straight lines, which suggests that a highly stable single complex is formed.

In the case of the slope ratio method, the ratio of slopes of the straight lines in Fig. 5 is found to be 2.14, confirming the formation of the complex containing nickel and RAPOX in the ratio 1 : 2, an inference drawn from Job's method.

Summary

RAPOX (resacetophenone oxime) in certain water-immiscible organic solvents is found to extract nickel from an aqueous medium as a nickel RAPOXimate complex. Cyclohexanone was found to be the best solvent for this

purpose. The brilliant green-coloured solution of the complex in cyclohexanone gave a maximum absorption at 600 mμ on a Beckman spectrophotometer DU. The coloured solution obeyed Beer's law in the lowest range—six parts per million. The extraction of this complex was quantitative in the pH range from 8 to 11.

The composition of the complex as determined by Job's method and the slope ratio method in a two-phase system was 1 : 2 (nickel to RAPOX). The back extraction study for the metal from the complex in the organic solvent was carried out and quantitative results obtained using an aqueous solution with a pH value below four.

The grateful thanks of the authors are due to Professor B. V. Thosar of the Tata Institute of Fundamental Research for making available the good working facilities of the Institute.

Tata Institute of Fundamental Research
Bombay-5, India (K. S. B. & A. T. R.)

Institute of Science
Bombay, India (M. B. K.)