

Complex Formation of Nickel(II) with Xylenol Orange

F. J. LANGMYHR and P. E. PAUS

University of Oslo, Chemical Institute A, Blindern, Oslo 3, Norway

The complex formation of nickel(II) with 3',3''-bis[[bis(carboxymethyl)amino]methyl]-5',5''-dimethylphenolsulfonephthalein or sodium salt (xylenol orange) was studied by spectrophotometry and potentiometric titration. Preliminary investigations of the ligand indicated that the preparations employed were pure and that the 3 components (xylenol orange, semixylenol orange, and an unidentified component) reported by Olson and Margerum to be present in commercial xylenol orange were simply a mixture of 3 proton complexes of the ligand.

At pH 3.00, a complex of 1 nickel atom and 1 xylenol orange molecule predominated in all mixtures, irrespective of the mole ratio between the reactants. The conditional constant (pH 3.00, 20°C, 0.1 M potassium chloride) was calculated to be 0.6×10^5 .

At pH 6.40, 2 species were detected; one, consisting of 1 nickel atom and 2 xylenol orange molecules, predominated in solutions containing an excess of the ligand; while the other, consisting of 2 nickel atoms and 2 xylenol orange molecules, predominated in mixtures containing the reactants in equimolar amounts or in the presence of an excess of the metal. The latter dimer compound is probably of the ring-formed type previously detected by Buděšinský in other metal xylenol orange systems.

Xylenol orange (in formulas abbreviated to XO) (3',3''-bis[[bis(carboxymethyl)amino]methyl]-5',5''-dimethylphenolsulfonephthalein or sodium salt) is applied as a metal indicator and as a reagent for the photometric determination of metals. The xylenol orange molecule contains a relatively high number of bond-forming groups, among which are two bidentate groups of carboxylic acid, each group being attached to different benzene rings. The properties of the ligand make it probable that the systems formed with metal ions contain several species. However, a study of the systems previously investigated showed that practically all authors had only detected 1 complex. More detailed studies of these systems can therefore be expected to reveal the presence of other compounds.

The present paper describes a photometric and potentiometric study of the complex formation of xylenol orange with nickel(II).

EXPERIMENTAL

Instruments. Extinction measurements were made with a Zeiss PMQ II spectrophotometer, a Beckman DB recording spectrophotometer and 1- and 5-cm glass cells.

For the potentiometric titrations and for the measurement and adjustment of pH a Beckman Zeromatic pH meter, with glass (pH 1–11) and calomel electrodes, was employed.

Reagents. The trisodium salt of xylenol orange was used in the photometric and potentiometric studies. In some preliminary investigations of the ligand the acid was employed. Both reagents were produced by Fluka, Switzerland.

For the photometric measurements standard solutions of nickel were prepared from the metal (Falconbridge Nikkelverk, Norway) which contained the following impurities (given in ppm): cobalt, about 200; zinc, 100; copper, 34; iron, 20; aluminium, 10; silicon, 10; and arsenic, 6.

For the potentiometric titrations the standard solutions of nickel were prepared from nickel(II) sulphate heptahydrate (Riedel-de Haën, Germany).

Investigations of the ligand. According to Olson and Margerum,¹ commercial xylenol orange may contain appreciable amounts of semixylenol orange and also a third, unidentified component.

In view of this statement it was found necessary to examine the reagent employed in the present investigation.

A paper chromatogram of xylenol orange (in the acid form) was prepared as specified by Olson and Margerum, the chromatogram confirmed the presence of 3 components.

The separation of xylenol orange and the third component from semixylenol orange by precipitation was tried as described by the above authors, but no precipitation took place.

A separation of the components by a cellulose column is also recommended by Olson and Margerum. Following the procedure of these authors, 3 fractions were again obtained. According to Olson and Margerum, fraction 1 is semixylenol orange. After having removed the eluent by vacuum distillation, fraction 1 was again passed through the cellulose column and it was also submitted to paper chromatography. Both methods showed again the presence of 3 fractions very much like those obtained in the first experiments.

A portion of xylenol orange was then diazotized with diazomethane according to a standard method.² The product was examined by paper chromatography using the above experimental conditions. The chromatogram exhibited only 1 spot, corresponding to the presence of only 1 component.

The conclusion was drawn, that the 3 spots or bands obtained by the paper or cellulose column chromatography of xylenol orange did not result from the presence of xylenol orange, semixylenol orange, and a third, unidentified component, but simply from 3 protonated forms of xylenol orange.

This conclusion is supported by the investigations of Řehák and Körbl,³ who calculated the distribution between the different protonated forms of xylenol orange as a function of pH. The diagram worked out by these authors shows that at pH 5 (the pH of the eluent) a solution of xylenol orange contains as predominating species the 3 proton complexes H_4XO^{2-} , H_3XO^{3-} , and H_2XO^{4-} .

Solutions. A standard solution of nickel (0.1 M) was prepared by dissolving 5.869 g of the metal in about 10 ml of concentrated nitric acid, transferring the solution to a 1000 ml volumetric flask and diluting to volume with water. From this solution other standard solutions were prepared by dilution.

Another standard solution of nickel (0.01 M) was prepared by dissolving in water 2.809 g of nickel(II) sulphate heptahydrate, previously dried to constant weight over calcium chloride. The solution was transferred to a 1000 ml volumetric flask and diluted to volume with water.

A standard solution of xylenol orange (0.1 M) was prepared by dissolving 0.1865 g of the trisodium salt in water, transferring the solution to a 250 ml volumetric flask and diluting to volume with water. The solution was not stored for more than 2 weeks.

The pH-meter was standardized with a 0.05 M solution of potassium hydrogen phthalate (pH 4.00 at 20°C), or a mixture of 0.025 M potassium dihydrogen phosphate and 0.025 M disodium hydrogen phosphate (pH 6.88 at 20°C).

The pH of the solutions was adjusted with either dilute hydrochloric acid or sodium hydroxide solution.

Ionic strength. During the photometric and potentiometric measurements, the ionic strength was kept relatively constant by maintaining a concentration of 0.1 M potassium chloride and low concentrations of ligand and metal ion.

Temperature. All measurements were made at room temperature, *i.e.* at $20^\circ \pm 3^\circ\text{C}$.

PHOTOMETRIC MEASUREMENTS

Absorption curves. Fig. 1 shows absorption curves at different pH values for solutions being 10^{-4} M with regard to both reactants. Similarly, Figs. 2 and 3 show the curves for mixtures having the nickel/xylenol orange ratios 5:1 and 1:5, respectively. All solutions were measured against blank solutions containing the same concentration of the ligand and adjusted to the same pH.

The absorption curves indicated that irrespective of the mole ratio between the reactants, the mixtures contained 2 species, one with absorption maximum

Fig. 1. Absorption curves at different pH values of 10^{-4} M solutions of nickel(II) and xylenol orange.

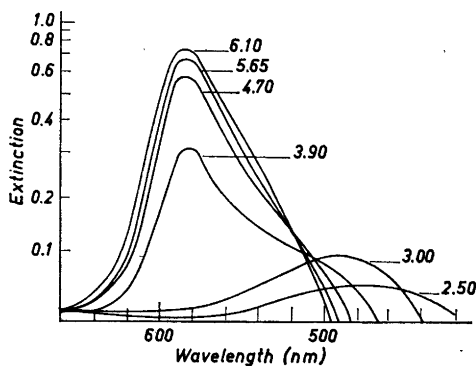
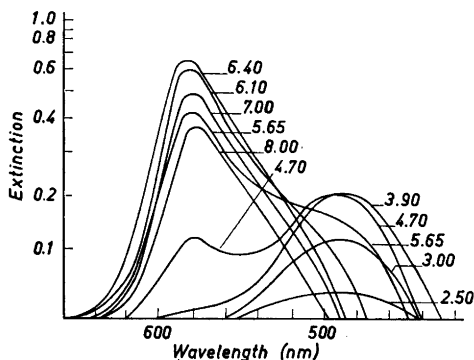


Fig. 2. Absorption curves at different pH values of solutions with the mole ratio nickel(II)/xylenol orange 5:1.

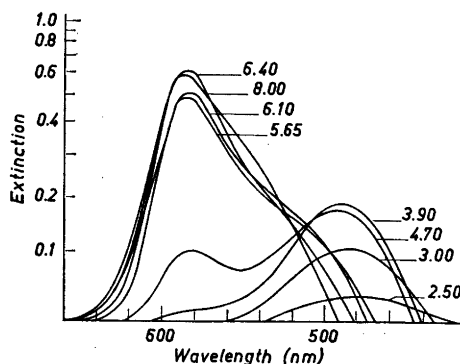


Fig. 3. Absorption curves at different pH values of solutions with the mole ratio nickel(II)/xylenol orange 1:5.

at 480 nm predominating at the lower pH values, and another with absorption maximum at 585 nm predominating in solutions maintained at higher pH values. It was further noted that the curve recorded at pH 8.00 for solutions having the mole ratio nickel/xylenol orange 1:5 exhibited a shoulder at about 550 nm. In solutions containing a tenfold excess of xylenol orange the shoulder also appeared at pH 6.40. On the basis of these preliminary investigations it was concluded that the system contained at least 2 species.

Investigations at pH 3.00. In order to establish the composition of the complex predominating at pH 3.00 the method of continuous variation, the molar ratio and the straight-line methods were employed.

Curves of continuous variation were plotted at the wavelength 480 nm for a series of solutions with a total, constant concentration of 5×10^{-4} M. The curve showed a maximum at the mole fraction 0.5, the curve branches had no inversion and the gradient at the end points was different from zero. This result clearly pointed to the presence of a complex with the composition 1:1.

A molar ratio curve was recorded at 480 nm for a series of solutions 10^{-4} M with regard to xylenol orange and containing varying amounts of nickel. The curve exhibited an intersection point at the mole ratio 1:1. Similarly, a curve was plotted at 480 nm for a series of solutions containing a constant amount of nickel and varying amounts of the ligand, but this curve did not give any distinct intersection point.

The straight-line method of Asmus⁴ with the modification introduced by Klausen and Langmyhr⁵ was then applied to a series of solutions containing a constant concentration of xylenol orange (10^{-4} M) and varying amounts of nickel, the concentration of the former reactant being maintained in excess. Presupposing a complex of the form $Ni_m(XO)_n$, this series gave the value $m = 1$. Similarly, a second series having a constant concentration of nickel (10^{-4} M) and varying amounts of the ligand, the concentration of nickel being kept in excess, gave a straight line for $n = 1$.

Finally, the straight-line method of Holme and Langmyhr⁶ was applied to a series of solutions in which the concentration of the ligand was 0.2×10^{-4} M, while the excess of nickel was varied. The curves plotted on the basis of measurements at 480 nm are shown in Fig. 4. Assuming again a complex of the form $Ni_m(XO)_n$, a straight line was obtained for $n/m = 1$.

The investigations at pH 3.00 clearly showed the predominance of a single species with the composition 1:1; this complex probably contains protons.

Investigations at pH 6.40. Curves of continuous variation were recorded at 585 nm of series of solutions with different total concentration. These curves are shown in Fig. 5.

At low mole fractions of nickel the curves in Fig. 5 show a gradient different from zero. In the mole fraction range $[C_{Ni}/(C_{Ni} + C_{XO})]$ 0.3 to 0.4 the curves exhibit an irregular form. The maxima appear at or near the mole fraction 0.5. At higher mole fractions the curves show an inversion and a parabolic approach to the end point.

The form of the curves at low mole fractions showed that the predominating species contained 1 nickel atom. The position of the maximum indicated a

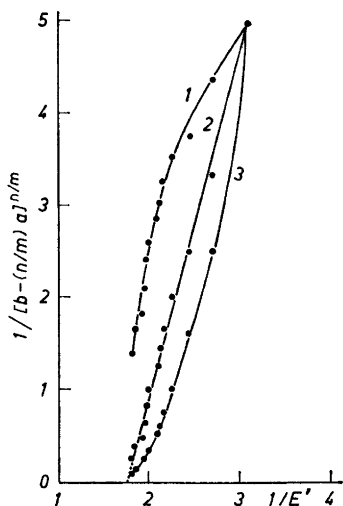


Fig. 4. Curves from the use of the straight-line method of Holme and Langmyhr. Constant concentration of xylenol orange 0.2×10^{-4} M. pH = 3.00. Wavelength 480 nm. Curve 1: $n/m = \frac{1}{2}$ (ordinate units to be multiplied by the factor 1.393); Curve 2: $n/m = 1$; Curve 3: $n/m = 2$ (ordinate units to be multiplied by the factor 2.500).

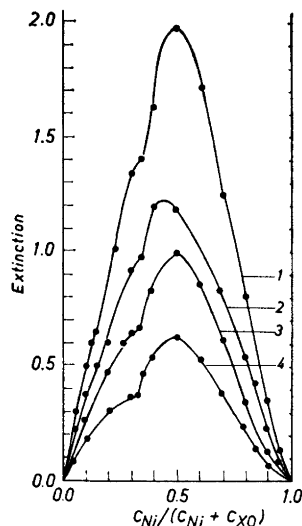


Fig. 5. Curves of continuous variation recorded at 585 nm for a series of solutions with different total concentration. pH = 6.40. Curve 1: 1.2×10^{-4} M; Curve 2: 0.8×10^{-4} M; Curve 3: 0.6×10^{-4} M; Curve 4: 0.4×10^{-4} M.

complex with the mole ratio 1:1, while the form of the curves at higher mole fractions of nickel showed a complex with more than 1, probably 2, ligand molecules.

The curves of continuous variation recorded at pH 6.40 could only be explained by assuming the presence of 2 complexes.

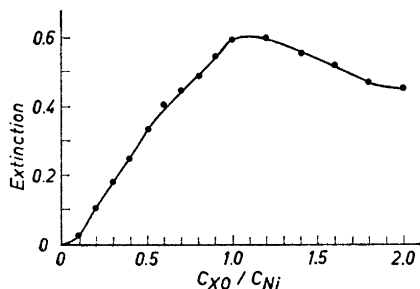


Fig. 6. Molar ratio curve recorded at 585 nm. Constant concentration of nickel 0.2×10^{-4} M. pH = 6.40.

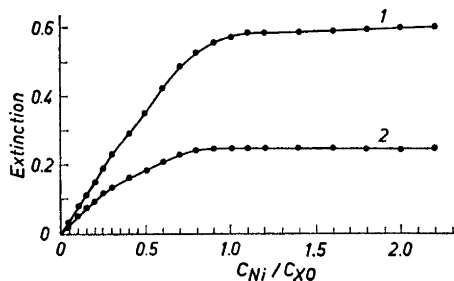


Fig. 7. Molar ratio curves recorded at 585 nm (Curve 1) and 550 nm (Curve 2). Constant concentration of xylenol orange 0.2×10^{-4} M. pH = 6.40.

For the use of the molar ratio method 2 series of solutions were prepared, one with a constant concentration (0.2×10^{-4} M) of nickel and varying concentrations of xylenol orange, and another with a constant concentration (0.2×10^{-4} M) of the ligand and varying concentrations of the metal.

The former series was measured at 585 nm and gave the curve reproduced in Fig. 6, while the latter series was measured at 550 and 585 nm, giving the curves shown in Fig. 7.

As seen from Fig. 6, solutions containing nickel in excess give a curve which approaches the end point parabolically, this form of the curve being in accordance with that of the right end branches in Fig. 5. This part of the curve again indicated the presence of a complex with more than 1 ligand molecule. The maximum in Fig. 6 appears at the mole ratio 1:1. At higher molar ratios the extinction decreases, probably due to the formation of another species.

The curves in Fig. 7 exhibit end branches without parabolic parts, this again corresponding to the form of the left end branches of the curves in Fig. 5. For mixtures containing an excess of the ligand, the curves in Fig. 7 show 2 intersection points. It was found difficult to extract any definite conclusions from these curves, apart from the obvious one that 2 or more species were present.

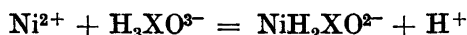
Finally, the straight-line method of Asmus⁴ was applied to a series of solutions containing a constant concentration of nickel (0.2×10^{-4} M) and varying amounts of the ligand, the former reactant being maintained in excess. The extinctions were measured at 585 nm. Assuming a complex of the form $Ni_n(XO)_n$, the method gave a value of $n = 2$.

POTENTIOMETRIC TITRATIONS

A mixture of 25 ml of a 10^{-3} M solution of the ligand and 5 ml of 0.0531 N hydrochloric acid was titrated with a 0.0490 N sodium hydroxide solution. Likewise, solutions containing 25 ml of a 10^{-3} M ligand solution, 5 ml of 0.0531 N hydrochloric acid, and 12.5, 25, and 50 ml of a 10^{-3} M solution of the metal were titrated with the standard alkali.

The ligand curve showed inflections after the addition of 3 and 4 equivalents of base added, this result being in accordance with that reported previously by Řehák and Körbl.³

The curves recorded (these are not reproduced) for the different mixtures of the reactants did not exhibit any distinct inflection points and very little information could be extracted from them. However, the curves for solutions containing the reactants in equimolar amounts or an excess of the ligand indicated that at pH about 4 the following reaction took place:



In the solution containing an excess of the metal, the titration resulted in the precipitation of nickel(II) hydroxide.

RESULTS

The composition of the complexes. The experimental data showed the presence of 3 species.

At pH 3.00 a complex of 1 nickel atom and 1 xylenol orange molecule predominated in all mixtures, irrespective of the mole ratio between the reactants. At pH 3.00 this complex probably contained 3 protons.

At pH 6.40 2 compounds were detected. A complex of 1 nickel atom and 2 xylenol orange molecules predominated in solutions containing an excess of the ligand, while in mixtures being equimolar or containing an excess of the metal, a complex of 2 nickel atoms and 2 xylenol orange molecules predominated. The structure of the ligand makes it probable that the latter, dimer complex is of the ring-formed type previously detected in the systems of xylenol orange with scandium(III), bismuth(III), thorium(IV) and other metal ions.⁷⁻⁹ For the different present complexes the properties of the ligand make a relatively large number of structural formulas possible; these are, however, not surveyed.

The stability of the complexes. The conditional constant at pH 3.00 of the 1:1 complex was calculated with the experimental data from the use of the straight-line method of Holme and Langmyhr⁶ and the directions given by these authors. The conditional constant (valid at pH 3.00, at 20°C and in the presence of 0.1 M potassium chloride) was calculated to be 0.6×10^5 . The stability of the other species was not calculated.

REFERENCES

1. Olson, D. C. and Margerum, D. W. *Anal. Chem.* **34** (1962) 1299.
2. Gattermann, L. and Wieland, H. *Die Praxis des organischen Chemikers*, 40th Ed., Walter de Gruyter & Co., Berlin 1961, p. 235.
3. Řehák, B. and Körbl, J. *Collection Czech. Chem. Commun.* **25** (1960) 797.
4. Asmus, E. *Z. anal. Chem.* **178** (1960) 104.
5. Klausen, K. S. and Langmyhr, F. J. *Anal. Chim. Acta* **28** (1963) 501.
6. Holme, A. and Langmyhr, F. J. *Anal. Chim. Acta. In the press.*
7. Buděšínský, B. *Collection Czech. Chem. Commun.* **28** (1963) 1858.
8. Buděšínský, B. *Z. anal. Chem.* **188** (1962) 266.
9. Buděšínský, B. and Bezděková, A. *Z. anal. Chem.* **196** (1963) 172.

Received May 31, 1966.