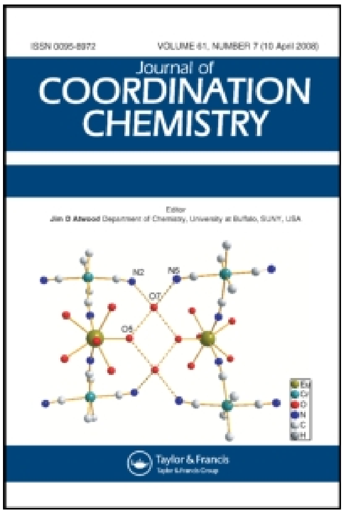

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A Spectrophotometric Study of Complexation Between Nickel(II) and 4-(5'-Methyl-3'-Isoxazolylazo)Resorcinol

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NOTE

A SPECTROPHOTOMETRIC STUDY OF COMPLEXATION BETWEEN NICKEL(II) AND 4-(5′-METHYL-3′-ISOXAZOLYLAZO)RESORCINOL

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The complexation equilibria between Ni(II) and 4-(5′-methyl-3′-isoxazolylazo)resorcinol have been spectrophotometrically studied in a 20% (v/v) ethanol-water medium at 0.1 M $NaClO_4$ ionic strength and species NiHR ($\log \beta_{111} = 14.83 \pm 0.05$), NiR ($\log \beta_{101} = 9.32 \pm 0.04$) and NiR_2 ($\log \beta_{102} = 17.84 \pm 0.05$) are established.

Pyridylazo- and thiazolylazophenol derivatives have been widely used as analytical reagents for several metal ions[1–2] but there is little reference in the literature to azo derivatives containing different heterocycles. Only in a few cases have the equilibria involved been studied. For these reasons, some isoxazolylazophenols have been synthesized and their complexation equilibria with several metal ions studied.[3–5]

We report here formation constants for complexes between Ni(II) and 4-(5′-methyl-3′-isoxazolylazo)resorcinol.

EXPERIMENTAL

A 10^{-3} M 4-(5′-methyl-3′-isoxazolylazo)resorcinol solution in absolute ethanol was used as the ligand source.[6] Standard 10^{-1} M $Ni(ClO_4)_2$ solution was prepared from the nitrate by perchloric acid treatment, and standardized complexometrically. Ionic strength was kept constant at 0.1 M ($NaClO_4$). Analytical reagent grade chemicals and deionized water were used throughout with no further purification.

The pH measurements were carried out with a Radiometer PHM64 digital pH-meter with glass-calomel combination electrode. Absorbance measurements were made using a Hitachi Perkin-Elmer 200 recording spectrophotometer provided with 1 cm matched quartz cells. Measurements were performed at 25 ± 0.1°C. Calculations were carried out on a Digital VAS/VMX 11/780 (V.4.0.) computer.

RESULTS AND DISCUSSION

Solutions containing nickel(II) and 4-(5′-methyl-3′-isoxazolylazo)resorcinol, are

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orange, λ_{max} 465 nm, at a 60-fold excess of nickel with pH > 4. However, in excess reagent solutions, the absorption maximum is at 460 nm and has a greater intensity. These results indicate the existence of at least two different complex species in solution.

The absorbance–pH curves at 465 nm for solutions with different C_{Ni}/C_R ratios indicate the formation of different complex species according to the experimental conditions.

The stoichiometry, as determined at 465 nm and pH 7.5 by continuous variation and mole ratio methods when C_R is constant, shows the presence of 1:1 Ni : R complex species, but a mole ratio method, when C_{Ni} is constant, does not give a definite composition for the species in solution.

The experimental data were analysed by applying the LETAGROP-SPEFO[7] numerical calculation method, and divided into two blocks; 1: curves with nickel ion in excess, and 2: curves with equimolar and excess reagent. Finally, the whole of the experimental data were studied together.

TABLE I

Values of U, σ(A), log β_{pqr} and ε_{pqr} for the different models tested by the LETAGROP-SPEFO program ($pM + qH + rR \rightleftharpoons M_pH_qR_r$).

Species	U	σ(A)	log β_{pqr}	ε_{pqr}[a]
a) metal ion excess solutions				
NiHR	0.854	0.095		
NiR	0.736×10^{-1}	0.027		
NiHR	0.180×10^{-2}	0.005	14.71 ± 0.07	4,320 ± 111
NiR			9.20 ± 0.06	34,351 ± 40
NiHR	0.240×10^{-2}	0.005		
NiR				
NiH_qR_2				
NiHR	0.265×10^{-2}	0.006		
NiR				
NiOHR				
NiHR	0.266×10^{-2}	0.006		
NiR				
$Ni_pH_qR_r$				
b) equimolar and reagent excess solutions				
NiHR	0.758	0.195		
NiR				
NiHR	0.350×10^{-1}	0.034		
NiR				
$NiHR_2$				
NiHR	0.547×10^{-3}	0.004	14.71 ± 0.07	4,320 ± 111
NiR			9.20 ± 0.04	34,351 ± 40
NiR_2			17.82 ± 0.06	69,277 ± 349
c) all data included				
NiHR	0.302×10^{-2}	0.005	14.83 ± 0.05	3,008 ± 133
NiR			9.32 ± 0.04	34,328 ± 54
NiR_2			17.84 ± 0.05	69,146 ± 226

[a] $M^{-1} cm^{-1}$.

From the results presented in Table I it can be seen that, for the curves when nickel ion is in excess, the model simultaneously including species NiHR and NiR fits experimental data much better than models containing only one species. Calculations for other models assuming, in addition to the NiHR, NiR complexes, the formation of Ni:R = 1:2, hydroxo or polynuclear species did not converge.

In contrast, results obtained for the curves for equimolar and excess reagent indicate that the NiHR, NiR and NiR_2 three species model not only fits the restricted experimental data (equimolar ratio and reagent excess) with minimum values of U and $\sigma(A)$, but in fact the whole of the experimental data. The values of the formation constants calculated for the NiHR, NiR and NiR_2 species are included in Table I.

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