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# Mechanism of Complex Formation: Kinetics and Equilibria of the Nickel(II)–Salicylate Ion System

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Rate and equilibrium measurements have been performed on the nickel(II)–salicylate ion system in the pH range between 6 and 7.2 at 25 °C and at an ionic strength 0.1 M. Under the experimental conditions a 1:1 chelate complex is formed with release of a proton. The equilibrium constant of the reaction is $1.4 \times 10^{-6}$. Temperature-jump experiments show that two parallel paths involving $Ni^{2+}$ and $NiOH^+$ ions, respectively, are operative. The rate constant of the path involving $Ni^{2+}$ ion ($70\ M^{-1}\ s^{-1}$) lies ca. 3 orders of magnitude below the value predicted by the Eigen mechanism whereas the species $NiOH^+$ reacts with a rate constant of $6.3 \times 10^4\ M^{-1}\ s^{-1}$. The results are discussed in terms of an attack by the two species of Ni(II) at the internally hydrogen-bonded carboxylic oxygen of salicylate ion.

## Introduction

The kinetics of formation of nickel(II) complexes have been so widely investigated that it is conceivable that Ni(II) will take over the central role in inorganic reaction mechanisms which has been occupied by Co(III) in the past. These reactions are in general discussed in terms of the Eigen mechanism[1,2] according to which the rate-determining step is solvent loss from the inner solvation shell of the metal after an external ion pair between metal and ligand has been formed.

Values of the second-order rate constants different from those expected on the basis of the simple $S_N1_{ip}$ model are sometime obtained when the ligand is a chelating agent.[3] These deviations from the normal behavior are often ascribed to rate-determining ring closure[3] and in some cases to the presence in the ligand of internal hydrogen bonds which make the reaction site blocked by a proton.[3-5] In a previous paper[6] on rates of complexation of nickel(II) with anthranilate, salicylate, and sulfosalicylate ions the abnormally low rates have been explained with the possibility of a steric-controlled mechanism.

In this study of the equilibria and kinetics of the nickel(II)–salicylate system we present different conclusions.

## Experimental Section

All chemicals were analytical grade reagents. Nickel perchlorate and salicylic acid were crystallized twice from water. Conductivity water was used to prepare the solutions and as a reaction medium. The desired acidities were obtained by adding to the solutions small amounts of $HClO_4$ or NaOH, and pH was measured with a Metrohm E 388 pH meter. Buffers of $NaH_2PO_4$–$Na_2HPO_4$ or trisethanolamine were avoided because we found that they reacted with Ni(II).

The ionic strength was 0.1 M ($NaClO_4$) in all kinetic runs and 0.3 M in the equilibrium measurements. The temperature was 25 °C.

Equilibrium results were obtained at 340 and 330 nm with a Perkin-Elmer 200 spectrophotometer and kinetic results at 615 nm by using a temperature-jump apparatus (Messanlagen-Studiengesellschaft, Göttingen). Blank experiments with solutions containing only nickel ion and indicator showed no relaxation effects in the time range of the experiments. The values of the relaxation times obtained from replicated runs exhibited a spread of ±10% at most. The concentrations of the reactants were changed from $10^{-3}$ to $10^{-2}$ M, and the indicator, bromothymol blue, was present in concentrations (1.5 or 3) × $10^{-5}$ M.

## Results

**Equilibrium Constant.** Evidence for formation of a complex between nickel(II) and salicylate ion has been obtained both by potentiometry and by spectrophotometry.

Titration curves have been performed with salicylic acid alone and in the presence of an equivalent concentration of nickel perchlorate. The comparison showed that complex formation begins at pH 6, and the degree of complexation increases with decreasing the hydrogen ion concentration. Above pH 7.7 subsequent additions of dilute NaOH did not lead to further increase of pH but to formation of a precipitate which was immediately revealed by a nonconstant instrument signal and became clearly visible after few minutes. Great care was taken to avoid local formation of precipitate since this is difficult to dissolve.

In the wavelength range between 310 and 350 nm the absorbance, $A$, of a mixture of salicylic acid and nickel perchlorate is higher than the sum of the contributions of the two components. If we ascribe this to formation of 1:1 complexes, it is possible to define an equilibrium ratio[5] (eq 1),

$$K = [NiL_T][H^+]/[Ni_f][L_f] \qquad (1)$$

where $[L_f]$ and $[Ni_f]$ are the sum of concentrations of all uncomplexed forms of ligand and nickel(II), respectively, and $[NiL_T]$ is the sum of the concentrations of all possible 1:1 complexes. The salicylate ion concentration, $C_L$, was $8 \times 10^{-4}$ M, and the nickel concentration, $C_{Ni}$, was changed between 0.050 and 0.091 M with pH varying between 6 and 7.2. Under these conditions it is assumed that $[H_2L] \ll [HL^-] \simeq [L_f]$ and that $[NiOH^+] \ll [Ni^{2+}] \simeq [Ni_f] \simeq C_{Ni}$, and the relationship between the absorbance, $A$, and the concentrations can be written in the form of eq 2, where $\Delta\epsilon = \epsilon_{NiL} - \epsilon_L - \epsilon_{Ni}$.

$$\frac{C_L}{A - \epsilon_L C_L - \epsilon_{Ni} C_{Ni}} = \frac{1}{\Delta\epsilon} + \frac{1}{\Delta\epsilon}\frac{1}{K}\frac{[H^+]}{C_{Ni}} \qquad (2)$$

The three $\epsilon$ values are mixed coefficients formed by the contributions of differently protonated forms of the components of the system and might therefore depend on pH. $\epsilon_L$ and $\epsilon_{Ni}$ have been independently determined and at the investigated acidities. Plots of the left-hand-side member of eq 2 against $[H^+]$ at different, constant, $C_{Ni}$ yield straight lines with a common intercept and the same $K$.

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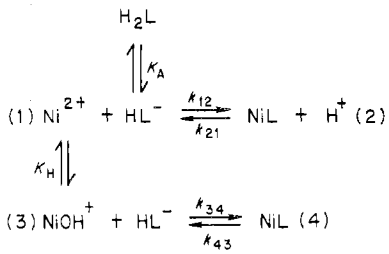
**Scheme I**



The linearity of these plots and the constant value of $\epsilon_{NiL}$ show that only one complex is indeed formed, namely, the chelate NiL, and the presence of monoprotonated forms can be neglected. Nonnegligible amounts of $NiHL^+$ should change the above-mentioned plots into curves exhibiting an upward curvature. Again, curves instead of straight lines should be obtained by plotting of the data according to eq 2 when the presence of higher order complexes makes itself felt.

Once it is established that only the chelate complex NiL is present in equilibrium with the reactants and $H^+$, the value of $K$ was obtained from the ratio between the intercept and slope of the graph shown in Figure 1 in which spectrophotometric data at 340 nm are reported. The least-squares line yields $K = (1.1 \pm 0.4) \times 10^{-6}$. A value in agreement with this has been derived from data at 330 nm. For our calculations we have converted the value at an ionic strength of 0.3 M into $1.4 \times 10^{-6}$ ($\mu = 0.1$ M) with the aid of the Davies equation.[7]

**Rate Constants.** A reaction scheme in agreement with the temperature-jump experiments and with the equilibrium results is given by Scheme I. A possible reaction between $NiOH^+$ and $H_2L$ cannot be separated from path (1)–(2). However, it has been ruled out since the protonated $H_2L$ would have to be more reactive than the $HL^-$ ion toward $NiOH^+$ in order to give a noticeable contribution to the overall rate.

When $\delta \equiv \delta[NiL]$, the expression for $1/\tau$ is given by eq 3. By making use of the inequalities $[H^+] \ll K_A$ and $[H^+]$

$$\frac{1}{\tau} = k_{12}\left\{[Ni^{2+}]\left(-\frac{\delta[HL]}{\delta}\right) + [HL^-]\left(-\frac{\delta[Ni]}{\delta}\right)\right\} + k_{34}\left\{[NiOH^+]\left(-\frac{\delta[HL]}{\delta}\right) + [HL^-]\left(-\frac{\delta[NiOH]}{\delta}\right)\right\} + k_{21}\left\{[H^+] + [NiL]\left(\frac{\delta[H]}{\delta}\right)\right\} + k_{43} \quad (3)$$

$\gg K_H$ one gets eq 4, where $\gamma \equiv 1 + C_{in}K_{in}/(K_{in} + [H^+])^2$ is

$$\frac{\delta[H]}{\delta} = \frac{1}{\gamma + [HL^-]/K_A + [NiOH^+]/[H^+] + K_w/[H^+]^2} \quad (4)$$

a measure of the contribution of the coupled acid–base reaction involving the indicator (in) to the buffering of the system. In addition, the following relationships (eq 5–7) have been obtained. The values of the dissociation constants used in these

$$-\frac{\delta[HL]}{\delta} = 1 + \frac{[HL^-]}{K_A}\frac{\delta[H]}{\delta} \quad (5)$$

$$-\frac{\delta[NiOH]}{\delta} = \frac{[NiOH^+]}{[H^+]}\frac{\delta[H]}{\delta} \quad (6)$$

$$-\frac{\delta[Ni]}{\delta} = 1 - \frac{[NiOH^+]}{[H^+]}\frac{\delta[H]}{\delta} \quad (7)$$

calculations are $K_A = 2.04 \times 10^{-3}$ M,[8] $K_H = 3.8 \times 10^{-10}$ M,[9] $K_{in} = 9.0 \times 10^{-8}$ M,[10] $K_w = 1.58 \times 10^{-14}$ M$^2$,[11] and $K = 1.4 \times 10^{-6}$ and all are referred to 25 °C and ionic strength $\mu = 0.1$ M.

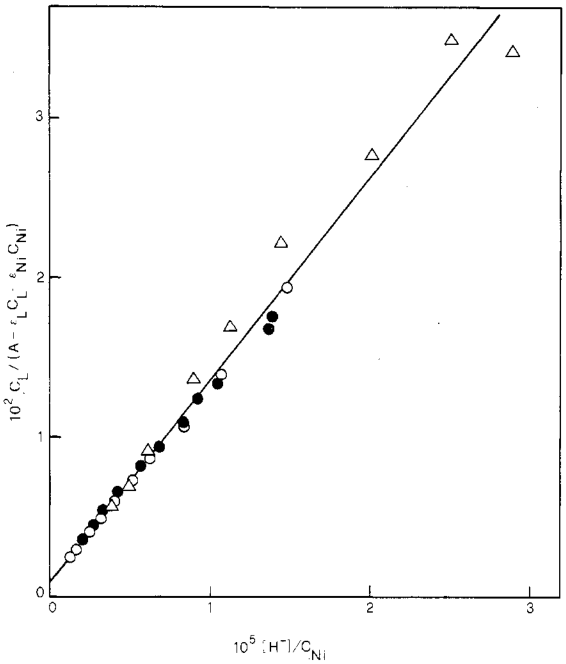


**Figure 1.** Values of $C_L/(A - \epsilon_L C_L - \epsilon_{Ni}C_{Ni})$ as a function of $[H^+]/C_{Ni}$ ($C_L = 8 \times 10^{-4}$ M, $\lambda = 340$ nm, 25 °C, $\mu = 0.3$ M): triangles, $C_{Ni} = 5.0 \times 10^{-2}$ M; solid circles, $C_{Ni} = 7.0 \times 10^{-2}$ M; open circles, $C_{Ni} = 9.1 \times 10^{-2}$ M.

Since $k_{12}/k_{21} = K$ and $k_{34}/k_{43} = K/K_H$, eq 3 can be written in the form

$$\frac{1}{\tau B} = k_{12} + k_{34}\frac{C}{B} \quad (8)$$

where

$$B \equiv [Ni^{2+}]\left(-\frac{\delta[HL]}{\delta}\right) + [HL^-]\left(-\frac{\delta[Ni]}{\delta}\right) + \frac{[H^+] + [NiL](\delta[H]/\delta)}{K} \quad (9)$$

and

$$C \equiv [NiOH^+]\left(-\frac{\delta[HL]}{\delta}\right) + [HL^-]\left(-\frac{\delta[NiOH]}{\delta}\right) + \frac{K_H}{K} \quad (10)$$

A plot of the data on the basis of eq 8 is shown in Figure 2. From the intercept of the least-squares line one obtains $k_{12} = 70 \pm 15$ M$^{-1}$ s$^{-1}$ and from the slope $k_{34} = (6.3 \pm 1.0) \times 10^4$ M$^{-1}$ s$^{-1}$. These values, together with the appropriate equilibrium constants, give $k_{21} = 5.0 \times 10^7$ M$^{-1}$ s$^{-1}$ and $k_{43} = 17.0$ s$^{-1}$.

## Discussion

The value of the equilibrium constant $K$ can be compared with the value of $3.8 \times 10^{-7}$ at 20 °C and $\mu = 0.15$ M derived from data reported in the literature.[12] The value of $k_{12}$ for a "normal" reaction can be calculated from the appropriate ion-pairing constant,[2] $K_{ip}$, and the rate of exchange, $k_{H_2O}$, between bulk water and the coordination shell of nickel(II) ion.[13] Taking into account a statistical factor[6,14] of 0.2, one obtains $0.2K_{ip}k_{H_2O} = 1.4 \times 10^4$ M$^{-1}$ s$^{-1}$, a value higher than the experimental value by a factor of 200. The discrepancy increases if a statistical factor such as 0.75 is used.[15] Our value of $k_{12}$ is also lower than that reported by Williams and Petrucci[6] by about 2 orders of magnitude. This difference is too high to be ascribed to the fact that in deriving the ex-

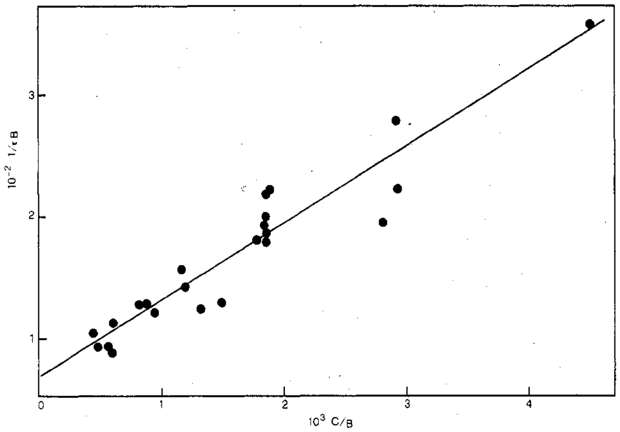


**Figure 2.** Plot of $1/\tau B$ against $C/B$ according to eq 8 at 25 °C and $\mu$ = 0.1 M.

pression for $1/\tau$ we have also taken into account the effect of the acidity and the additional path with $NiOH^+$ ion, and, moreover, the concentrations have been computed by using our equilibrium constant. A plot of $1/\tau$ against $\sum C$ as in ref 6 yields a straight line with a slope higher than the value of $k_f$ of Williams and Petrucci by a factor of 4 and with negative intercept.

It should be noted that we worked at higher acidities because any attempt to perform measurements in the vicinity of pH 8, as these authors did, failed due to precipitate formation. The abnormally low value of the rate constant $k_{12}$ can be explained in two ways: (a) the rate-controlling step is the closure of the ring with simultaneous or subsequent expulsion of the proton,[3] (b) a fast equilibrium between a hydrogen-bonded and an "open" form of the ligand is preceding the reaction with the metal ion.[3,5] According to hypothesis (a), metal ion and ligand react at a "normal" rate giving rise to a monodentate intermediate which is in turn converted to the chelate. Reaction (1)–(2) can therefore be represented by

$$\underset{(1)}{Ni^{2+}} + HL^- \underset{k_{31}}{\overset{k_{13}}{\rightleftarrows}} \underset{(3)}{NiHL^+} \underset{k_{23}}{\overset{k_{32}}{\rightleftarrows}} \underset{(2)}{NiL} + H^+$$

The fact that the species $NiHL^+$ has not been detected in the equilibrium measurements means that the inequality [NiL] ≫ [$NiHL^+$] holds in the entire range of investigated pH. Moreover, since only one relaxation time has been observed, the concentration of the monodentate complex must be vanishingly small. It should be noted, on the other hand, that all carboxylate ions give 1:1 complexes with nickel(II) with stability constants ranging between 1 and 10 $M^{-1}$ ($K$ = 6.3 $M^{-1}$ for the Ni(II) 2-methoxybenzoate complex).[12] An explanation of the fact that the value of $K_{13}$ lies far below these limits can be found in the high stabilization of the salicylate ion produced by formation of an internal hydrogen bond between the phenolic proton and the carboxylic oxygen. In addition, the possibility of chelate formation helps to make negligible the concentration of the monodentate complex.

According to hypothesis (b), a conformational equilibrium between a hydrogen-bonded form, $HL^-$, and an "open" form, $*HL^-$ (with an equilibrium constant $K_*$), of salicylate ion is rapidly established. If only the open form reacts at a "normal" rate, then the experimental $k_{12}$ is equal to $K_*$ $(0.2K_{ip}k_{H_2O})$, if $K_* \ll 1$.

However, since the conformational equilibrium is presumably unaffected by a change of the cation, the reactions of salicylate ion with all cations must be slower by a factor $K_*$ if the only reactive form is the open $*HL^-$, whereas complex formation reactions of aluminum(III)[8] and iron(III)[16] ion with salicylate ion proceed at normal rates. For this reason we tend to discount this possibility.

Again in the framework of hypothesis (b), a direct attack of the metal ion on the hydrogen-bonded oxygen can be considered. In this case the reactivity of the ligand is expected to change from one metal ion to another and for a given hydrolizable metal ion is expected to increase with increasing the number of OH groups bonded to the central atom. This is in line with the high value of the rate constant of the path involving the basic $NiOH^+$ ion whose reactivity exceeds that of the $Ni^{2+}$ ion by a factor of $10^3$. This explanation has already been advanced to interpret the mechanism of the reactions of nickel(II)[4,5] and magnesium[17] ions with internally hydrogen-bonded ligands. We also tend to favor this idea with respect to hypothesis (a) first because no sign of rate-determining ring closure was found in the reaction of Al(III) with salicylate which is "normal" and with the reaction of more labile Fe(III) and Ga(III).[18] Second, if the rate of reaction is controlled by factors of steric nature, there is no reason why the path involving $NiOH^+$ should show such a high increase in rate unless the enhanced reactivity is ascribed to the labilizing effect produced by $OH^-$ on the water molecules remaining in the coordination shell of nickel(II) ion.[19] But if this effect (of which no NMR evidence has so far been given) were present, the contribution of $NiOH^+$ to the observed rates of complexation should have made itself felt in all investigations carried out at pH values above 6. Since this is not the case, we conclude that the "normal" reactivity of $NiOH^+$ cannot be much higher than that of $Ni^{2+}$, whereas its basic properties play the major role in the reactions where the displacement of a proton blocking the reaction site is a necessary requisite.

**Registry No.** $Ni(OH_2)_6^{2+}$, 15365-79-4; salicylate ion, 63-36-5.

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