

Kinetics of Complexation of Ni(II) with N,N'-Ethylene disalicylamide in Alkaline Media and Effect of Cationic Surfactant on the Rate of Reaction

B. NAYAK and S.D. BHATTAMISRA*

Department of Chemistry

Berhampur University, Berhampur-760 007, India

The kinetics of formation reaction of N,N'-ethylene disalicylamidato nickelate(II) is followed at 30°C in alkaline media. A bell-shaped pH-rate profile is obtained indicating a maximum at pH = 9.5. The active species near the maximum are the hydrated Ni(II) species and the deprotonated species of the ligand. The rate constant for formation decreases with increase in concentration of cetyl trimethyl ammonium bromide (CTAB). This results from partitioning of the hydrophobic ligand in the micellar pseudophase and electrostatic repulsion between the metal and the micellar surface.

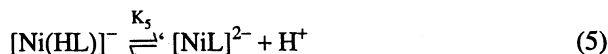
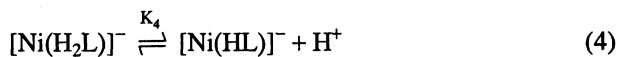
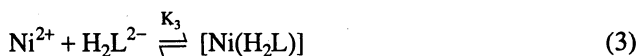
Key words: Kinetics, complexation, Ni(II), cationic surfactant, rate of reaction

INTRODUCTION

In previous studies of nickel(II) complex of N,N'-ethylene disalicylamide^{1,2}, it was possible to obtain structural information of the chelates formed, equilibrium constants for all microscopic reaction steps and the reactivity of the complexes towards substitution by polydentate carboxylates, by combining potentiometric pH-measurements with infrared and spectral studies. Such studies also revealed interesting similarities with most nickel peptides³. Dissociation reactions in deprotonated peptide complexes of nickel have been studied in great detail and are believed to proceed through one of the two reaction pathways⁴. However, the kinetic aspect of the metal ion interaction in the formation of the metal chelate has largely been ignored. The present paper deals with the kinetic and mechanistic study of the formation of N,N'-ethylene disalicylamidato nickelate(II), $[\text{NiL}]^{2-}$, in alkaline media. The complex $[\text{NiL}]^{2-}$ has two phenolate oxygens and two deprotonated amide nitrogens in a square-planar arrangement around Ni(II) and this makes the study important as the phenolate groups are known to be effective metal ion carriers in biological systems⁵. The effect of a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), on the reaction rate has also been included in the study in order to examine the relative importance⁶ of bulk and interfacial reactions in the complexation process.

EXPERIMENTAL

All the chemicals used were of AR grade. Preparative methods for the ligand and the complex are described elsewhere^{1,7}. The ligand is a white amorphous solid soluble in alcohol and acetone. It was identified as *N,N'*-ethylene disalicylamide (H_4L) with m.f. $C_{16}H_{16}N_2O_4$ from elemental analysis, IR, NMR and spectral studies. The complex $K_2[NiL]$ is an orange yellow solid, hygroscopic in nature and highly soluble in water. Its m.f. was found to be $K_2NiC_{16}H_{12}N_2O_4$ using information from similar analytical and spectral studies. For the dissociation constants of the ligand and the stability constants of the nickel complexes, data from pH-metric studies conform to the following equilibria:



with $pK_1 = 8.29$, $pK_2 = 9.70$, $\log K_3 = 2.96$, $pK_4 = 7.79$ and $pK_5 = 7.75$. The closeness in values of pK_4 and pK_5 suggests loss of both amide protons in a single step⁸. Hence, in the present study, equilibrium in eqn. (6) is considered for the formation of the doubly deprotonated nickel complex NiL^{2-} instead of eqns. (4) and (5).



The kinetics of formation of $[NiL]^{2-}$ was studied spectrophotometrically using Shimadzu-160A UV-visible spectrophotometer under pseudo-first order conditions by following the appearance of $[NiL]^{2-}$ at 440 nm ($\epsilon = 285 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in 50% ethanol-water medium at 30°C. The ionic strength was maintained at 0.15 mol dm^{-3} with KNO_3 . The pH was adjusted by adding requisite amount of standard KOH solution, the volume being ascertained from a blank pH-metric run containing different reactant solutions at the specified experimental condition. In the pH-range studied from 8 to 11, the predominant nickel and ligand species were Ni^{2+} , $NiOH^+$, H^3L^- and H^2L^{2-} . CTAB was twice recrystallised from methanol-diethyl ether. The critical micelle concentration was measured by conductimetry⁹ and the value was obtained as 0.95×10^{-3} . Equal volumes of surfactant solution were added separately to calculate the amount of nickel nitrate and ligand solution before start of the reaction.

RESULTS AND DISCUSSION

Two rate steps were observed in the kinetic study of Ni(II) reaction with the

ligand H_4L in the pH range from 8 to 11. Both steps are dependent on pH and the initial concentration of the ligand. The slow step is completed in almost an hour preceded by a fast step of 60 to 120 seconds duration. It is the fast step which is considered here. The fast reaction is consistent with the rate law

$$\frac{d[NiL^{2-}]}{dt} = k_{obs}[Ni^{2+}] \quad (7)$$

Table-1 lists the k_{obs} values at various concentrations of the metal ion and the ligand as well as at different pH. At constant pH, k_{obs} vs. $[H_4L]_T$ gives a straight line passing through the origin. Thus the possibility of any complex dependence of rate on $[H_4L]_T$ is ruled out; rather the fast step probably is a reaction leading to equilibrium which is attained slowly in the succeeding step prolonged for 1 h or so. The dependence of rate constant on $[H_4L]_T$ is thus given by

$$k_{obs} = k[H_4L]_T \quad (8)$$

The variation of k_{obs} with pH is shown in Fig. 1. The pH profile shows a

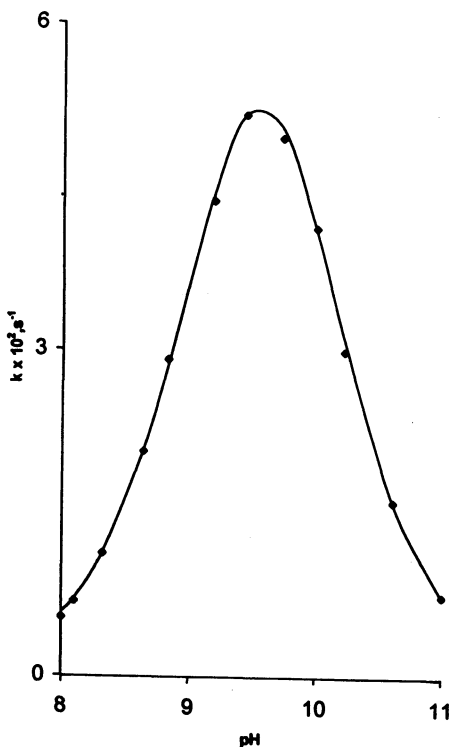
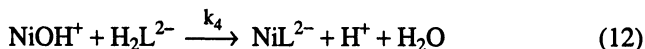
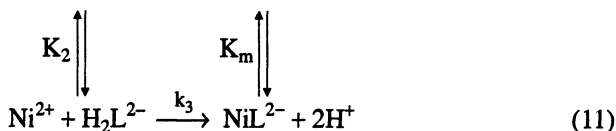
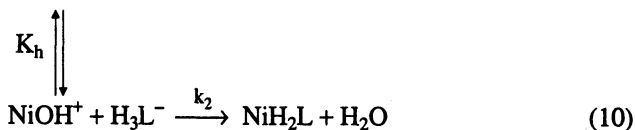


Fig.1. Variation of k with pH as per data in Table-1. The solid line is drawn with calculated rate constant values (k_{cal}) and \blacklozenge = observed rate constant values (k_{obs}).

maximum at pH = 9.5 which is almost equal to half the sum of $(pK_h + pK_2)$.¹⁰ The variation of solvent composition or ionic strength has no significant effect on the rate of reaction. The complexation process resulting from the interaction of the metal ion with ligand species is given by the following reactions:



where K_h is the hydrolysis constant of Ni^{2+} ($\text{p}K_h = 9.4$), K_2 is the second dissociation constant of the ligand H_4L ($\text{p}K_2 = 9.7$) and K_m corresponds to the equilibrium constant as given in eqn. (6). At constant pH, the rate equation is

$$F_2 \frac{d[\text{NiL}^{2-}]}{dt} = \frac{T_{\text{Ni}} - [\text{NiL}^{2-}]}{F_3} F_2 \times \frac{[\text{H}_4\text{L}]_T F_4}{F_1} \quad (13)$$

where $F_1 = 1 + K_2/[\text{H}^+]$

$$F_2 = ([\text{H}^+]^2/K_m) + 1$$

$$F_3 = (K_h/[\text{H}^+]) + 1$$

$$F_4 = k_1 + (k_2 K_h/[\text{H}^+]) + (k_3 k_2/[\text{H}^+]) + (k_4 K_h k_2/[\text{H}^+]^2)$$

and T_{Ni} and $[\text{H}_4\text{L}]_T$ are the total metal ion and ligand concentrations respectively. Integrating equation (13),

$$\ln \frac{[\text{NiL}^{2-}]_\infty}{[\text{NiL}^{2-}]_\infty - [\text{NiL}]_t} = k_{\text{obs}} t$$

where $[\text{NiL}^{2-}]_\infty$, proportional to absorbance, is the concentration of the species at infinite time and $[\text{NiL}^{2-}]_t$ is the concentration of the same species at any time t . From eqns. (13) and (14) it follows that

$$k_{\text{obs}} = [F_4/(F_3 \times F_1)][h_4\text{L}]_T \quad (15)$$

which coupled with eqn. (8) yields

$$k' = F_4/(F_3 \times F_1) \quad (16)$$

The values of the different microrate constants are analysed using eqn. (16) and are found to be $k_1 = 4.22 \times 10^{-3}$, $k_2 = 5.389$, $k_3 = 7.552$ and $k_4 = 1.466 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Alternatively, k_1 and k_4 can be calculated from the two edges of the bell-shaped pH profile by assuming that reactions (9) and (11) respectively are only operative under such conditions. Table-1 lists the calculated rate constant values at different concentrations of the ligand and at different pH. The agreement between the experimental and calculated rate constant values supports the reaction scheme.

TABLE-1
RATE CONSTANT VALUES FOR THE Ni(II) REACTION WITH N,N'-ETHYLENE
DISALICYLAMIDE (H₄L) AT 30°C

I = 0.125 mol dm⁻³, solvent: ethanol-water (50% v/v)

pH	10 ³ [Ni ²⁺] _T /mol dm ⁻³	10 ³ [H ₄ L] _T /mol dm ⁻³	10 ² k _{obs} /s ⁻¹	10 ² k _{cal} /s ⁻¹ *	
8.57 ± 0.03	1.00	1.67	1.927		
	1.33		1.880		
	1.67		1.935		
	2.00		1.934		
	2.33		1.900		
	1.33		0.67	0.864	0.777
			1.00	1.148	1.166
			1.33	1.600	1.551
			1.67	1.937	1.944
			2.00	2.243	2.332
	2.33	2.732	2.721		
7.90	1.33	1.67	0.409	0.468	
8.00			0.532	0.581	
8.10			0.682	0.703	
8.32			1.126	1.133	
8.64			2.073	2.088	
8.83			2.917	2.863	
9.19			4.376	4.461	
9.44			5.158	5.167	
9.73			4.951	5.038	
10.00			4.125	4.093	
10.22			2.994	3.097	
10.61			1.612	1.598	
11.00			0.747	0.735	

*Calculated using eqn. (15): $k_1 = 4.22 \times 10^{-3}$, $k_2 = 5.389$, $k_3 = 7.552$ and $k_4 = 1.466 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹. pK_h = 9.7 and pK₂ = 9.4

Owing to their solubilising properties, micelles can incorporate reactant molecules in their hydrophobic core and thus affect the rate of reaction in solution. There are two categories of sources for effects: (i) the change in polarity of the microenvironment may influence the passage of the reacting system, and (2) solubilisation can affect the absolute and relative concentrations of reacting species¹¹. In the case of cationic surfactants, if the ligand is very hydrophobic and thus strongly partitioned in the micellar pseudophase and considering the metal ions are repelled by the electrostatic potential on the micellar surface, then in the extreme case, the complexation reaction will not occur at all. Table-2 lists the k_{obs} values for the Ni(II)-H₄L reaction at different concentrations of the cationic surfactant CTAB. Although the complexation reaction does occur, there is a systematic decrease in the rate constant values. This can be interpreted by considering the micellar effect to be a pure concentration effect. There is an increased partitioning of the ligand in favour of the micellar pseudophase and if

the actual complexation reaction is assumed to take place in the bulk aqueous phase, the rate constant obviously falls. However, the contribution of any interfacial reaction through formation of species like $[\text{Ni}(\text{Br})_4^{2-}]$ cannot be ruled out.

TABLE 2
RATE CONSTANT VALUES FOR THE REACTION OF
Ni(II) WITH ETHYLENE DISALICYLAMIDE (H_4L)
AT DIFFERENT CONCENTRATIONS OF CTAB

$I = 0.125 \text{ mol dm}^{-3}$, temp. = 30°C , pH = 9.19,
 $[\text{Ni(II)}]_{\text{T}} = 1.33 \times 10^{-3}$ and $[\text{H}_4\text{L}]_{\text{T}} = 1.67 \times 10^{-2} \text{ mol dm}^{-3}$

$[\text{CTAB}] \times 10^2 \text{ mol dm}^{-3}$	$k_{\text{obs}} \times 10^2/\text{s}^{-1}$
0.87	3.451
1.30	3.224
1.73	3.109
2.17	2.994
2.60	2.764

REFERENCES

1. S.D. Bhattamisra, S.R. Misra and S. Tripathy, 5th International Conference on Mechanism of Reactions in Solution, Kent, England (1990).
2. S.D. Bhattamisra and S. Tripathy, *J. Chem. Soc., Dalton Trans.*, 1907 (1993).
3. M.K. Kim and A.E. Martell, *J. Am. Chem. Soc.*, **89**, 5138 (1967).
4. W.R. Kennedy and D.W. Margerum, *Inorg. Chem.*, **24**, 2490 (1985).
5. A.E. Frost, H.H. Freedman, S.J. Westerbock and A.E. Martell, *J. Am. Chem. Soc.*, **80**, 530 (1958).
6. C. Tondre, S.G. Son and M. Hebrant, *Langmuir*, **9**, 950 (1993).
7. H. Ojima and Kaishi, *Nippon Kagaku*, **88**, 329.
8. K.S. Bai and A.E. Martell, *J. Am. Chem. Soc.*, **91**, 4412 (1969).
9. M. Hebrant and C. Tondre, *Colloids and Surfaces A*, **83**, 293 (1994).
10. J.E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd Edn., Harper International, Cambridge, p. 295 (1983).
11. R.D. Vold and M.J. Vold, *Colloid and Interface Chemistry*, Addison- Wesley, London, p. 660 (1983).

(Received: 3 September 2001; Accepted: 5 November 2001)

AJC-2506