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Kinetics and Mechanism of Complex Formation of Nickel(II) with 1-(2-Pyridylazo)-2-naphthol in Acetic Acid[1)]

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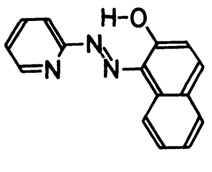
The complex formation reactions of nickel(II) nitrate, nickel(II) acetate, and nickel(II) chloride with 1-(2-pyridylazo)-2-naphthol (PAN) in acetic acid (HOAc) to form the 1:1 nickel(II)–PAN complex have been studied kinetically by using a stopped-flow technique. The second-order rate constants and activation parameters at 25 °C are $k=(1.4\pm0.1)\times10^4\ \mathrm{mol^{-1}\,kg\,s^{-1}}$, $\Delta H^{\neq}=51.2\pm1\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=6.4\pm4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta V^{\neq}=23.4\pm2.4\ \mathrm{cm^3\,mol^{-1}}$ for $Ni(NO_3)_2$, $k=(1.1\pm0.1)\times10^4\ \mathrm{mol^{-1}\,kg\,s,^{-1}}$, $\Delta H^{\neq}=49.5\pm1\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=-1.3\pm4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta V^{\neq}=15.5\pm2.6\ \mathrm{cm^3\,mol^{-1}}$ for $Ni(OAc)_2$, and $k=(4.8\pm0.1)\times10^4\ \mathrm{mol^{-1}\,kg\,s^{-1}}$, $\Delta H^{\neq}=51.4\pm1\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=17.0\pm4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta V^{\neq}=35.4\pm5.5\ \mathrm{cm^3\,mol^{-1}}$ for $NiCl_2$. The positive value of $\Delta V^{\neq}$ strongly suggests a dissociative mode of activation.

Kinetics of the complexation of nickel(II) ion has been studied extensively in aqueous solution and it has proved that the reactions proceed *via* the Eigen mechanism.[2–4)] On the other hand, studies in nonaqueous solvents are not numerous.[5–7)] Acetic acid has been utilized as a useful solvent in the titration of weak bases since Conant and Hall,[8)] and the acid-base equilibria in this solvent have been studied first by Kolthoff and Bruckenstein,[9a)] and later by Tanaka and Nakagawa.[9b)] There are not many studies on the complex formation of metal ions in acetic acid.[10)] We have recently reported the solvent-exchange rate on copper(II) acetate[11)] and manganese(II) perchlorate[12)] in acetic acid.

In this paper we describe the rates of reactions of nickel(II) species ($Ni(NO_3)_2$, $Ni(OAc)_2$, and $NiCl_2$) with 1-(2-pyridylazo)-2-naphthol (PAN or Hpan) in acetic acid. This is the first kinetic study on complex formation of a simple metal ion with an acyclic ligand in acetic acid.[13)]



PAN or Hpan

Experimental

Reagents. In order to keep the reaction medium as dry as possible, extreme care was taken in the purification and preparation of all reagents and compounds. All reagents and solutions were stored in a glove box or a desiccator.

Acetic Acid: The purification of acetic acid was described previously.[14)] The water content of acetic acid and acetic acid solutions was confirmed to be less than 5×10^{-3} mol kg^{-1} by the Karl-Fisher titration.

PAN: PAN (Dojindo Laboratories, Kumamoto) was purified by sublimation.

Nickel(II) Salts: Hydrated nickel(II) nitrate (reagent grade) was recrystallized from distilled water. The hydrate was dissolved in acetic acid containing a small amount of nitric acid. Acetic anhydride equivalent to the water involved was added to the nickel(II) nitrate solution. Anhydrous nickel(II) nitrate precipitates. The precipitate was washed with acetic anhydride and then with acetic acid. This compound is formulated as $Ni(NO_3)_2\cdot6HOAc$.[15)] The crystals of nickel(II) acetate and nickel(II) chloride were prepared similarly and solvated salts may be formulated as $Ni(OAc)_2\cdot4HOAc$ and $NiCl_2\cdot4HOAc$. Each nickel solution was prepared by dissolving these crystals in acetic acid.

Lithium Salts: Reagent grade lithium perchlorate, lithium nitrate, and lithium chloride were recrystallized from distilled water and dried at 170, 130 and 120 °C respectively. Perchloric acid solution and lithium acetate were prepared by the methods described previously.[10)]

Measurements. A highly sensitive spectrophotometer (SM 401, Union Giken Co. Ltd., Osaka) and a Carl Zeiss spectrophotometer (Model PMQ II) were used for the measurements of absorption spectra. Reaction rates at atmospheric pressure were measured by means of a highly sensitive stopped-flow spectrophotometer.[10,16)] The temperature of the reaction cell was maintained to within ±0.1 °C. At high-pressures up to 55 MPa the reactions were followed by using a high-pressure stopped-flow apparatus.[17)] At 25 °C acetic acid freezes at 55 Mpa.

Equilibria in Acetic Acid. In acetic acid almost all substances exist as the non-dissociating form because of its low dielectric constant ($\varepsilon=6.18$ at 20 °C).[18)] Thus it is important to consider separately the ionization and dissociation. Overall dissociation of AB is expressed by Eq. 1.

$$\mathrm{AB} \overset{K_i}{\rightleftharpoons} \mathrm{A^+B^-} \overset{K_d}{\rightleftharpoons} \mathrm{A^+ + B^-} \tag{1}$$

An overall dissociation constant K_D is defined by Eq. 2.

$$K_D = \frac{[\mathrm{A^+}][\mathrm{B^-}]}{[\mathrm{AB}]+[\mathrm{A^+B^-}]} = \frac{K_iK_d}{1+K_i}, \tag{2}$$

where K_i is an ionization constant and K_d is a dissociation constant.[9a)] Available values of K_D are $10^{-12.53}$ for H_2O,[19)] $10^{-10.1}$ for HNO_3,[20)] $10^{-8.55}$ for HCl,[9a)] $10^{-5.87}$ for $HClO_4$,[21)] $10^{-6.79}$ for LiOAc,[21,22)] $10^{-7.1}$ for LiCl,[21,23)] $10^{-5.80}$ for $LiClO_4$,[24)] and $10^{-7.63}$ for $Ni(OAc)_2$ ($Ni(OAc)_2 \rightleftharpoons NiOAc^+ + OAc^-$).[25)] K_d can be calculated by an equation of the type derived by Fuoss and Kraus for ion-pair formation,[26)] at least to a correct order of magnitude. The K_d value is estimated to be about 10^{-6} mol dm^{-3} for all of these 1:1 electrolytes. Then values of K_i are estimated to be $10^{-6.5}$ (H_2O), $10^{-4.1}$ (HNO_3), $10^{-2.5}$ (HCl), $10^{-0.7}$ (LiOAc), $10^{-1.1}$ (LiCl), and $10^{-1.6}$ ($Ni(OAc)_2$).

From the K_i value of $Ni(OAc)_2$, it may be concluded that two OAc^- ions in $Ni(OAc)_2$ exist in the first coordination sphere of nickel(II). Since the Edwards E_n value[27)] (the electron-donating property) of chloride ion (1.24) is similar to that of

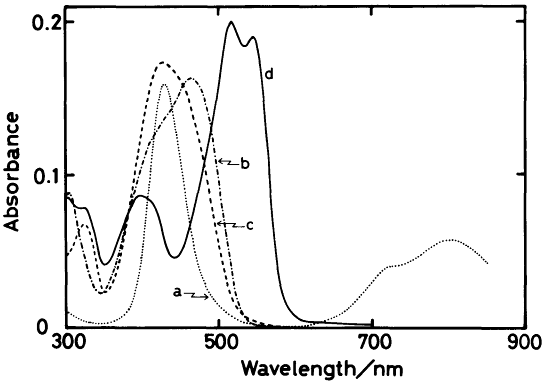


Fig. 1. Absorption spectra of nickel(II) chloride, the acid and base forms of PAN, and the nickel(II)–PAN complex in acetic acid.
a: $[NiCl_2]=1.12\times10^{-2}$ mol kg^{-1}; b: $[PAN]=9.43\times10^{-6}$ mol kg^{-1}; c: $[PAN]=9.43\times10^{-6}$ mol kg^{-1}, $[HClO_4]=5.5\times10^{-5}$ mol kg^{-1}; d: $[PAN]=9.43\times10^{-6}$ mol kg^{-1}, $[Ni(OAc)_2]=2.02\times10^{-4}$ mol kg^{-1}.

acetate ion (0.95), two chloride ions in $NiCl_2$ are thought also to be in the first coordination sphere of nickel(II). The absorption spectra of nickel(II) nitrate, acetate, and chloride in acetic acid show their typical octahedral geometry (see Fig. 1-a for $NiCl_2$).[28] The molar absorption coefficients of nickel(II) solutions are independent of concentration of nickel(II) salts. The complexation rate of $Ni(NO_3)_2$ does not change even in the presence of HNO_3 up to 10^{-3} mol kg^{-1} (*vide infra*). These facts are consistent with solvolysis of nickel(II) salts not occurring in acetic acid.

The addition of perchloric acid (the strongest acid) to an acetic acid solution of PAN changes PAN to its acid form (see Fig. 1), protonated at nitrogen of the pyridyl group of PAN, while the addition of lithium acetate, the strongest base, causes little change in the absorption spectrum. From the change of the spectra the mole fraction of ionized PAN $([HpanH^+OAc^-]+[HpanH^+])/[Hpan]$ is estimated to be about 0.05 at most. Thus PAN exists practically as the base

$$\mathrm{Hpan} + \mathrm{HOAc} \rightleftharpoons \mathrm{HpanH^+OAc^-} \rightleftharpoons \mathrm{HpanH^+} + \mathrm{OAc^-} \qquad (3)$$

form (Hpan) in acetic acid.

Absorption spectrum was measured for mixtures of the 2×10^{-5} mol kg^{-1} PAN solution with the 2×10^{-5} to 2×10^{-3} mol kg^{-1} nickel(II) solution. At the nickel(II) concentration higher than 2×10^{-4} mol kg^{-1}, the complexation of PAN is quantitative and the reverse reaction can be neglected. The reaction system is expressed by Eq. 4.

$$\mathrm{Hpan} + \mathrm{NiX_2} \longrightarrow \mathrm{Ni(pan)X} + \mathrm{HX}, \qquad (4)$$

where X^- is NO_3^-, OAc^-, or Cl^-. The spectrum of the 1 : 1 nickel(II)-PAN complex is shown in Fig. 1-d. The pan$^-$ ion is a tridentate ligand. The 1 : 1 nickel(II)-PAN complex tends to decompose slowly with half-life of several hours.

Results and Discussion

Kinetic measurements were carried out at 516, 544, and 554 nm for $Ni(NO_3)_2$, at 516 nm and 544 nm for $Ni(OAc)_2$, and 516 nm and 540 nm for $NiCl_2$ in large excess nickel concentration over PAN. The change in absorbance at each wavelength as a function of reaction time was satisfactorily fitted to the pseudo-first-order rate law. A conditional first-order rate constant k_0 involving the nickel(II) concentration was obtained by the relation: $\ln(A_\infty-A_t)=\ln(A_\infty-A_0)-k_0t$, where A_0, A_t, and A_∞ denote the absorbances at initial time, at time t, and at infinite time, respectively.

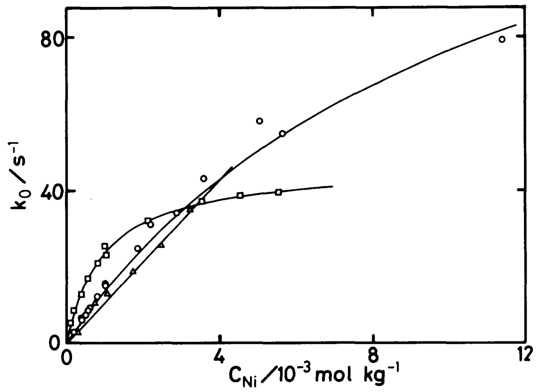


Fig. 2. Conditional first-order rate constant k_0 as a function of the nickel(II) concentration C_{Ni}.
○: $Ni(NO_3)_2$; △: $Ni(OAc)_2$; □: $NiCl_2$.
Each point is an average of several determinations. The solid curves are calculated with the constants obtained.

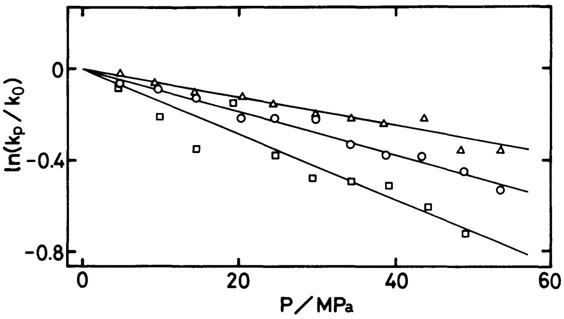


Fig. 3. Pressure dependence of ln k at 25.0 °C.
○: $Ni(NO_3)_2$; △: $Ni(OAc)_2$; □: $NiCl_2$.
Each point is an average of several determinations. The straight lines are calculated by using the ΔV^* values in Table 2.

The rate of formation of the 1 : 1 nickel(II)-PAN complex is first order with respect to PAN. Conditional first-order rate constants under various conditions are summarized in Table 1. The plots of k_0 against the nickel(II) concentration are given in Fig. 2. The effect of water in acetic acid on k_0 was checked by the addition of various amounts of water up to 6×10^{-2} mol kg^{-1}. Though k_0 decreases slightly with increasing water concentration, the presence of water up to 5×10^{-3} mol kg^{-1} does not affect the rate. At lower concentrations of the nickel(II) the data show a linear relationship through the origin and then $k_0=kC_{Ni}$, where k is a second-order rate constant and C_{Ni} is a total concentration of nickel(II). At higher C_{Ni} the data deviate from the straight line. This deviation will be considered later in detail.

The activation parameters obtained from the temperature dependence of k (17.0—35.0 °C), *i.e.* the Eyring plot, are tabulated in Table 2 . By the transition state theory, the relation between k and pressure P is given as $(\partial \ln k/\partial P)_T = -\Delta V^{\neq}/RT$. As apparent from Fig. 3, the rate constant varies linearly with pressure: the activation volume, $\Delta V^{\neq}$, is independent of pressure. The values of $\Delta V^{\neq}$ are also summarized in Table 2.

Since the reactions of $Ni(NO_3)_2$ and $NiCl_2$ with PAN produce HNO_3 and HCl, respectively, the effect of these acids on the reaction rate was examined. When these acids are added to the acetic acid solution of PAN, PAN changes into an acid form. From the change of the absorption spectra, the equilibrium constants of Eq. 5, $K_{PAN\text{-}HX}$, were calculated to be 4.3×10^2 mol^{-1} kg for HNO_3 and 4.2×10^4 mol^{-1} kg for HCl.

$$\mathrm{Hpan} + \mathrm{HX} \overset{K_{\mathrm{PAN\text{-}HX}}}{\rightleftharpoons} \mathrm{HpanH^+X^-} \qquad (5)$$

Moreover under conditions where $[Ni(NO_3)_2]=2.04\times10^{-3}$ mol kg^{-1} and $[PAN]=1.15\times10^{-5}$ mol kg^{-1}, the presence of 100-fold excess of HNO_3 over [PAN] did not affect the reaction rate as expected from the $K_{PAN\text{-}HNO_3}$ value. Under conditions where $[NiCl_2]=2.60\times10^{-4}$ mol kg^{-1} and $[PAN]=1.15\times10^{-5}$ mol kg^{-1}, the addition of HCl twice as much as PAN decreased the reaction rate by *ca.* 6%. After all the reaction rate is not affected by HNO_3 or HCl generated by the complexation.

The addition of various amounts of lithium perchlorate and lithium acetate to a PAN solution resulted in the change in the spectra with an isosbestic point at 456 nm. The reaction corresponds to equilibrium 6.

$$\mathrm{Hpan} + \mathrm{Li^+ClO_4^-} + \mathrm{HOAc} \rightleftharpoons \mathrm{HpanH^+ClO_4^-} + \mathrm{LiOAc} \qquad (6)$$

TABLE 1. CONDITIONAL FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF NICKEL(II) WITH PAN

T / °C	$[PAN]\times10^5$ / mol kg^{-1}	$C_{Ni}\times10^4$ / mol kg^{-1}	k_0 $^{a)}$ / s^{-1}	
		$Ni(NO_3)_2$		
25.0	4.31	5.65	8.34±0.21	(5)
25.0	4.31	28.4	34.2 ±0.3	(9)
25.0	4.31	56.5	55.0 ±0.7	(8)
25.0	4.31	114	79.3 ±1.4	(5)
25.0	4.31	199	103 ±2	(5)
25.0	4.31	338	121 ±1	(10)
25.0	0.986	2.03	2.96	(1)
25.0	0.986	4.05	6.16±0.03	(3)
25.0	0.986	5.08	7.56±0.11	(4)
25.0	0.986	6.11	9.24±0.13	(4)
25.0	0.986	8.14	12.1 ±0.2	(5)
25.0	0.986	10.2	14.9 ±0.1	(5)
25.0	4.30	4.03	6.46±0.13	(5)
25.0	4.30	10.1	15.5 ±0.1	(9)
25.0	4.30	22.0	31.1 ±0.5	(8)
25.0	4.30	35.8	43.1 ±0.8	(5)
25.0	4.30	50.5	58.1 ±0.4	(4)
17.0	4.44	18.6	13.0 ±0.2	(7)
20.0	4.44	18.6	17.0 ±0.2	(8)
25.0	4.44	18.6	24.8 ±0.4	(5)
30.0	4.44	18.6	35.0 ±0.4	(7)
35.0	4.44	18.6	47.8 ±0.4	(6)
		$Ni(OAc)_2$		
25.0	0.990	2.88	2.78±0.08	(4)
25.0	4.31	10.8	12.9 ±0.2	(5)
25.0	4.31	17.4	18.7 ±0.6	(5)
25.0	4.31	24.8	25.6 ±0.9	(5)
25.0	4.31	32.3	35.0 ±0.4	(5)
17.0	4.46	7.47	5.94±0.09	(6)
20.0	4.46	7.47	7.57±0.08	(4)
25.0	4.46	7.47	10.6 ±0.2	(7)
30.0	4.46	7.47	15.5 ±0.1	(6)
35.0	4.46	7.47	20.7 ±0.3	(6)
		$NiCl_2$		
17.0	0.983	1.98	4.46±0.11	(3)
17.0	0.983	4.02	6.40±0.03	(3)
17.0	4.27	10.0	12.7 ±0.2	(4)
17.0	4.27	35.5	17.9 ±0.3	(4)
17.0	4.27	55.4	19.2 ±0.3	(4)
25.0	0.971	0.989	5.25±0.08	(6)
25.0	0.971	1.92	8.62±0.25	(7)
25.0	0.971	3.96	12.6 ±0.3	(6)
25.0	0.971	5.59	16.9 ±0.1	(6)
25.0	0.971	8.20	21.0 ±0.5	(6)
25.0	0.971	10.4	23.0 ±0.7	(7)
25.0	4.27	9.96	25.4 ±0.3	(3)
25.0	4.27	35.4	37.3 ±0.6	(3)
25.0	4.27	45.5	38.8 ±0.4	(4)
25.0	4.27	55.4	39.6 ±0.2	(4)
30.0	0.983	1.98	12.5 ±0.2	(4)
30.0	0.983	4.02	20.0 ±0.7	(4)
30.0	4.27	10.0	35.3 ±0.4	(5)
30.0	4.27	35.5	56.9 ±0.6	(5)
30.0	4.27	55.4	62.1 ±0.4	(5)
35.0	0.983	1.98	18.5 ±0.2	(3)
35.0	0.983	4.02	29.8 ±0.6	(2)
35.0	4.27	10.0	51.3 ±0.7	(4)
35.0	4.27	35.5	91.6 ±0.4	(4)
35.0	4.27	55.4	93.5 ±1.6	(4)

a) Figures in parentheses (the last column) indicate the number of runs, and ± indicates the standard deviation.

TABLE 2. ACTIVATION PARAMETERS FOR THE COMPLEX FORMATION OF NICKEL(II) WITH PAN IN ACETIC ACID

Reaction	k(25 °C) / mol^{-1} kg s^{-1}	ΔH^{*} / kJ mol^{-1}	ΔS^{*} / J mol^{-1} K^{-1}	ΔV^{*} / cm^3 mol^{-1}
$Ni(NO_3)_2$+PAN	$(1.4\pm0.1)\times10^4$	51.2±1	6.4±4	23.4±2.4
$Ni(OAc)_2$+PAN	$(1.1\pm0.1)\times10^4$	49.5±1	−1.3±4	15.5±2.6
$NiCl_2$+PAN	$(4.8\pm0.1)\times10^4$	51.4±1	17.0±4	35.4±5.5

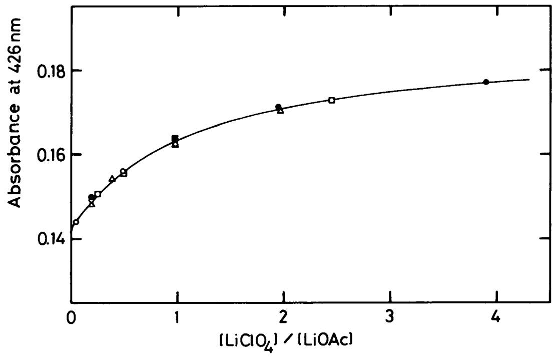


Fig. 4. Effect of lithium acetate and lithium perchlorate on spectra of PAN.
[PAN] = 1.53×10^{-5} mol kg^{-1}, [LiClO$_4$]/mol kg^{-1} = 1.59×10^{-4} (○); 3.17×10^{-4} (△); 7.90×10^{-4} (□); 3.16×10^{-3} (●).

Taking into consideration the ionization of PAN shown by Eq. 3, the equilibrium constant for Eq. 6 was determined to be $[\mathrm{HpanH^+ClO_4^-}][\mathrm{LiOAc}][\mathrm{Hpan}]^{-1}\times[\mathrm{Li^+ClO_4^-}]^{-1}=0.91\pm0.03$ by analyzing the change in absorbance at 426 nm (see Fig. 4). The similar phenomena have been reported previously.[29,30]

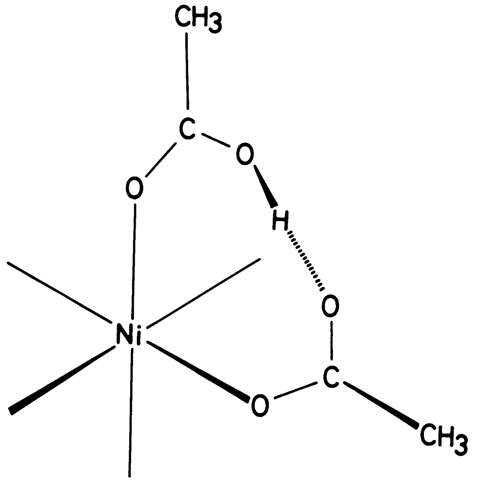
As apparent from Fig. 2, the plots for nickel(II) nitrate and nickel(II) chloride deviate from the straight line with increasing nickel(II) concentration. The deviation is thought to be due to a fast equilibrium in which PAN interacts with nickel(II) species to form a nonreactive species. The nonreactive species of PAN seems to be a quadrupole ion-pair of the acid form of PAN, similar to the species that Bruckenstein and Kolthoff have shown for Methyl Yellow.[31] It is reasonable that the extent of the deviation, *i.e.*, the ion-pair formation, parallels the ionization constants $K_{\mathrm{PAN\text{-}HX}}$ for HOAc,[32] $\mathrm{HNO_3}$, and HCl. The conditional first-order rate constant is given by the relation: $k_0=kC_{\mathrm{Ni}}/(1+KC_{\mathrm{Ni}})$, where K is a formation constant of a nonreactive ion-pair. The value of K for $\mathrm{Ni(NO_3)_2}$ is 92 mol^{-1} kg at 25.0 °C and those for $\mathrm{NiCl_2}$ are 1206, 1007, 927, and 842 mol^{-1} kg at 17.0, 25.0, 30.0, and 35.0 °C, respectively.

The reactivity of nickel(II) chloride is higher than the hexasolvento nickel(II) involved in the nitrate. This is just as expected from the following equation:[33]

$$\log k_{\mathrm{ML}}{}^{-\mathrm{S}} = \log k_{\mathrm{M}}{}^{-\mathrm{S}} + \gamma E(\mathrm{L}), \tag{7}$$

where $k_{\mathrm{ML}}{}^{-\mathrm{S}}$ and $k_{\mathrm{M}}{}^{-\mathrm{S}}$ denote the rate constants of solvent exchange at ML and M, respectively, $E(\mathrm{L})$ the electron donating ability of L, and γ a constant characteristic of the metal ion M.

As stated earlier, the electron donating ability (E_{n}) of chloride (1.24) is not much different from that of acetate (0.95). Although a similar enhancement of reactivity is expected for nickel acetate, nickel acetate is the least reactive among these three nickel species. This may be due to the coordination of acetate with nickel as a hydrogen bridged dimer bidentate as follows:[34]



Therefore the reactivity of the acetate is anticipated to be less than expected from its E_{n} value: we observe hardly the bound ligand effect for the acetate in its complexation in acetic acid. The E_{n} value for acetate (0.95) is not for the dimeric acetate but for the simple acetate.

The values of activation enthalpy are much the same for the present three systems (see Table 2). The parallel relation between ΔV^{*} and ΔS^{*} is observed. Since the activation volumes are positive and considerably large, these reactions are concluded to proceed via a dissociative-interchange mechanism. The dissociative character increases in the order: acetate<nitrate<chloride.

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