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Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. IV. Nickel(II) Malate and Nickel(II) Tartrate

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Kinetic and equilibrium measurements were carried out for the complexation reaction of nickel(II) malate and nickel(II) tartrate in an aqueous solution at 20 °C and at pressures up to 100 MPa. From the pressure dependence of the stability constant and the rate constant, the reaction volume, ΔV^0, and the activation volume, $\Delta V_f^\ddagger$, for the complex formation were estimated as follows: $\Delta V^0=17.8\pm0.6\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta V_f^\ddagger=13.8\pm0.6\,\mathrm{cm^3\,mol^{-1}}$ for nickel(II) malate, and $\Delta V^0=17.8\pm0.5\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta V_f^\ddagger=13.7\pm1.2\,\mathrm{cm^3\,mol^{-1}}$ for nickel(II) tartrate. Comparing the ΔV^0 values with those obtained for other carboxylate ligands, it was inferred that both malate and tartrate ions form a six-membered chelate complex coordinated by carboxyl and hydroxyl oxygens. The rate-determining step of the overall complexation reaction was assigned to the first bond formation process based on the $\Delta V_f^\ddagger$ value with the correction for the volume change associated with the outer-sphere complex formation.

A pressure-variable study of a chemical reaction provides information about the volume change associated with the reaction.[1)] The reaction volume and the activation volume are very useful parameters for understanding features of the reaction. We have been carrying out the kinetic and equilibrium measurements for the complexation reaction of nickel(II) with carboxylate ligands in an aqueous solution under pressure in order to interpret the course of the reaction through the volume profile.[2–4)] Along the line of this series of studies, in the present study we investigated the complexation reactions of nickel(II) malate and nickel(II) tartrate under various pressures up to 100 MPa. From the pressure dependence of the stability constants and the rate constants of the complexation reactions, the values of reaction and activation volumes were estimated and compared with those previously obtained for other carboxylate ligand systems.

Experimental

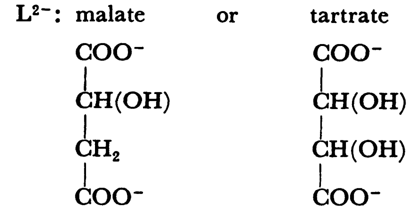
Stock solutions of nickel(II) malate and nickel(II) tartrate were prepared from nickel sulfate and corresponding acids by the same procedure as described previously.[2)] The concentration of the solution was determined by titrating with an EDTA solution standardized by a standard solution of zinc nitrate. Guaranteed grade reagents of nickel sulfate, L-malic acid, and DL-tartaric acid were obtained from Wako Pure Chemicals and used without further purification. Each sample solution was prepared by diluting the stock solution to the desired concentration. The pH's of the sample solutions were in the range of 6.1±0.2 for both nickel(II) malate and nickel(II) tartrate, where most of the ligands were considered to be in a fully dissociated form from the pK_a values of the acids; $pK_{a1}=3.28$ and $pK_{a2}=4.72$ for malic acid,[5)] and $pK_{a1}=2.80$ and $pK_{a2}=3.96$ for tartaric acid.[5)]

The stability constants of the complexes under various pressures were determined from conductivity measurements according to the Fuoss-Kraus method[6)] as described previously.[2,4)] The conductivity were measured for sample solutions of 20 different concentrations ranging from 2×10^{-4} to 1×10^{-3} mol dm^{-3} for nickel(II) malate and from 1×10^{-4} to 1.5×10^{-3} mol dm^{-3} for nickel(II) tartrate. A high-pressure pressure-jump apparatus[7)] was used for kinetic measurements under pressure. The pressure-jump measurements were made for sample solutions of 11—13 different concentrations ranging from 8×10^{-4} to 1×10^{-2} mol dm^{-3} for nickel(II) malate and from 5×10^{-4} to 2×10^{-3} mol dm^{-3} for nickel(II) tartrate. The observed relaxation process was characterized by a single relaxation time. The temperature was kept at 20.0±0.1 °C and the pressure was maintained within ±0.5 MPa of the designated pressure for both equilibrium and kinetic measurements. The concentration in the molarity scale was corrected for compression under pressure using the density data of water.[8)]

Results and Discussion

The complexation reaction under consideration is represented in Scheme 1.

$$\mathrm{Ni^{2+} + L^{2-} \overset{K}{\rightleftharpoons} NiL}$$



$$\mathrm{L^{2-}}:\ \text{malate} \begin{array}{c}\mathrm{COO^-}\\ |\\ \mathrm{CH(OH)}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COO^-}\end{array} \quad \text{or} \quad \text{tartrate} \begin{array}{c}\mathrm{COO^-}\\ |\\ \mathrm{CH(OH)}\\ |\\ \mathrm{CH(OH)}\\ |\\ \mathrm{COO^-}\end{array}$$

Scheme 1.

Stability constants of the complexes, K, determined from the conductivity data are listed in Table 1 (for details of the determination procedure, see Ref. 2). The reaction volume, ΔV^0, for the complexation reaction can be evaluated from the pressure dependence of the stability constant according to the relation[1)]

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta V^0 - RT\kappa_0, \tag{1}$$

where κ_0 represents the solution compressibility and other symbols have their usual meanings. In the above expression, $-RT\kappa_0$ is a correction term for the compression required when the concentration is expressed in terms of molarity and has a value of 1.1

Table 1. Stability Constants and Rate Constants for the Complexation Reaction of Nickel(II) Malate and Nickel(II) Tartrate as a Function of Pressure at 20 °C and I→0[a]

	Pressure/MPa					
	0.1	20	40	60	80	100
(a) Nickel(II) Malate						
$K/10^3\,\mathrm{mol^{-1}\,dm^3}$	7.99(0.85)	7.15(0.67)	6.18(0.55)	5.14(0.44)	4.46(0.35)	3.80(0.29)
$k_f/10^5\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	2.00(0.07)	1.82(0.07)	1.61(0.06)	1.44(0.07)	1.28(0.06)	1.09(0.04)
$k_d/10\,\mathrm{s^{-1}}$	2.50(0.28)	2.55(0.26)	2.60(0.25)	2.80(0.27)	2.86(0.26)	2.88(0.24)
(b) Nickel(II) Tartrate						
$K/10^3\,\mathrm{mol^{-1}\,dm^3}$	2.80(0.08)	2.35(0.06)	2.01(0.06)	1.71(0.06)	1.51(0.06)	1.30(0.06)
$k_f/10^5\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	2.61(0.05)	2.20(0.07)	1.99(0.06)	1.73(0.06)	1.60(0.06)	—
$k_d/10\,\mathrm{s^{-1}}$	9.33(0.32)	9.35(0.40)	9.90(0.43)	10.1(0.5)	10.7(0.6)	—

a) Standard deviations are shown in parentheses.

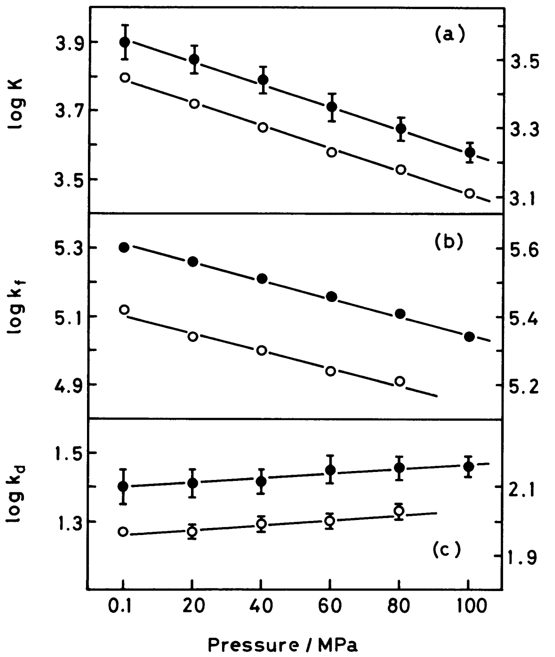


Fig. 1. Pressure dependence of (a) log$K$, (b) logk_f, and (c) logk_d at 20 °C: ●, nickel(II) malate (left scale); ○, nickel(II) tartrate (right scale). Solid lines show the linear least-squares fits to the data points.

cm^3 mol^{-1} [1a] for dilute aqueous solution as in the present case. Figure 1a shows plots of log$K$ against pressure for nickel(II) malate and nickel(II) tartrate. In the measured pressure range, log$K$ decreased linearly with increasing pressure. From the slope of the straight line fitted by a least-squares method, the values of reaction volume for the complexation reaction were estimated according to Eq. 1, and they are listed in Table 2 together with those obtained for other carboxylate ligands.

The rate constants for the complexation reaction were determined from the pressure-jump relaxation data according to the following relations; the details of the procedure were described elswhere.[2,4]

$$1/\tau = k_f[\gamma_{\pm}^2(c_{\mathrm{Ni}}+c_{\mathrm{L}}) + 1/K]$$
$$k_d = k_f/K, \qquad (2)$$

where τ represents the relaxation time, k_f and k_d the rate constants for the complex formation and dissociation at zero ionic strength, c_{Ni} and c_{L} the equilibrium concentration of nickel(II) and ligand ions, and $\gamma_{\pm}$ the mean activity coefficient of the free ions at a given ionic strength. The values of the rate constants at various pressures are summarized in Table 1. The activation volume of the complexation reaction was estimated from the pressure dependence of the rate constants based on a relation analogous to Eq. 1.[1] Plots of log k_f and log k_d against pressure are shown in Figs. 1b and 1c, respectively. In the measured pressure range, a linear relationship was obtained between the logarithm of the rate constant and the pressure. From the slope of the straight line, the values of the activation volume for the complex formation, ΔV_f^*, and dissociation, ΔV_d^*, were estimated. They are listed in Table 2 together with the activation volumes obtained for the complexation reaction with other carboxylate ligands.

It may be considered that the volume change associated with the complex formation in aqueous solution between metal ion and charged ligand consists of several contributions; i) the release of electrostriction due to the charge neutralization, ii) the elimination of solvated water around the coordinating group accompanied by the coordination bond formation, which produces free water, iii) the difference in coordination bond length between metal–water bond and metal-ligand bond, and iv) for chelating ligand, the increase of free volume, which is too small to be occupied by the solvent molecule, resulting from the formation of a ring structure. The contributions from i), ii), and iv) are positive for volume increase in the system, while the sign of the contribution from iii) may depend on the nature of the metal-ligand bond. According to the above consideration, it can be expected that the difference in the structure of the complex (e.g., monodentate or polydentate complex, or type of coordinating group(s) to metal ion) is reflected in the reaction volume.

The top five ligands in Table 2 have the same electrical charge(−2), and hence, the contribution i) is the same for these ligands. A succinate ion forms a

Table 2. Reaction Volumes, ΔV^0, and Activation Volumes, ΔV^*, for the Complex Formation of Nickel(II) with Carboxyl Ligands[a)]

Ligands	ΔV^0	$\Delta V^{\ddagger}_{\mathrm{f}}$	$\Delta V^{\ddagger}_{\mathrm{d}}$	$\Delta V^{\ddagger}_{\mathrm{f}}-\Delta V^0_{\mathrm{os}}$[b)]	Reference
Succinate	11.1±0.9	14.1±0.8	3.0±0.9	7.3	2
Malonate	13.5±1.0	14.7±0.5	1.2±1.2	7.5	4
Tartronate	13.3±0.7	15.2±0.5	1.9±0.8	8.0	4
Malate	17.8±0.6	13.8±0.6	−4.0±0.5	6.6	This work
Tartrate	17.8±0.5	13.7±1.2	−4.1±0.7	6.5	This work
Glycolate	17.3±1.0	14.7±0.5	−2.6±0.7	11.6	3
Lactate	17.6±0.9	13.5±0.4	−4.1±0.6	10.4	3

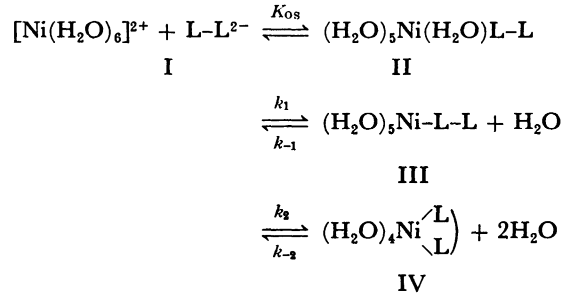
a) In $\mathrm{cm^3\,mol^{-1}}$; Errors are standard deviations estimated from the least-squares analysis. b) The values of ΔV^0_{os} estimated from the Hemmes equation[14] are as follows; $6.8\,\mathrm{cm^3\,mol^{-1}}$ for succinate at 10 °C, $7.2\,\mathrm{cm^3\,mol^{-1}}$ for malonate, tartronate, malate, and tartrate at 20 °C, and $3.1\,\mathrm{cm^3\,mol^{-1}}$ for glycolate and lactate at 20 °C.

monodentate complex rather than a seven-membered chelate complex,[9] while a malonate ion forms a six-membered chelate complex coordinated by two carboxyl oxygens.[10] This accords with a smaller ΔV^0 value for a succinate than for a malonate on considering the contributions ii) and iv). The similar ΔV^0 value for tartronate and malonate suggests that tartronate ion also forms a six-membered chelate complex by two carboxyl groups.[4]

Large ΔV^0 values for the complexation of nickel(II) malate and nickel(II) tartrate obtained in the present study indicate that malate and tartrate ions form a chelate complex with nickel(II). Some possible structures of the chelate complex are suggested from the molecular structure of malate and tartrate ions (shown in Scheme 1). Since a seven-membered chelate is unstable as seen in nickel(II) succinate, there remain two possibilities as a chelate structure; i.e., five-membered or six-membered ring coordinated by a carboxyl and a hydroxyl groups. The values of ΔV^0 for these two systems are quite similar, and they are also comparable to those for nickel(II) glycolate and nickel(II) lactate listed in Table 2. Glycolate and lactate ions form a five-membered chelate complex with nickel(II) by carboxyl and hydroxyl groups.[11,12] The similarity of ΔV^0 with glycolate and lactate systems might lead to the conclusion of a five-membered ring structure for nickel(II) malate and nickel(II) tartrate. However, the difference in the electrical charge between these two classes of ligands must be taken into account. Since glycolate and lactate ions have a charge of −1, the volume increase associated with charge neutralization (contribution i)) should be considerablly smaller than that for malate and tartrate ions. Thus, if nickel(II) malate and nickel(II) tartrate have a five-membered chelate ring, a somewhat larger ΔV^0 value should result rather than the observed value, because other contributions ii)—iv) may be regarded as to not differ significantly for these two classes of ligands. Hence, it may be considered that nickel(II) malate and nickel(II) tartrate form a six-membered chelate complex coordinated by carboxyl and hydroxyl groups.

The difference in ΔV^0 between malonate, tartronate systems and malate, tartrate systems, both of which form six-membered chelate complexes, may be attributed to the difference in coordinating groups. Since the interaction of a hydroxyl oxygen with a nickel(II) ion is weaker than that of a carboxyl oxygen, it may be expected that the bond length between a hydroxyl oxygen and a nickel(II) ion is longer than that between a carboxyl oxygen and a nickel(II) ion. Thus, larger ΔV^0 for malate and tartrate than malonate and tartronate can be partly explained in terms of contribution iii).

The metal complexation reaction has generally been interpreted in terms of a stepwise mechanism,[13] which can be represented by Scheme 2 for the bidentate chelate complex.



$$\underset{\mathrm{I}}{[\mathrm{Ni(H_2O)_6}]^{2+}} + \mathrm{L\text{-}L^{2-}} \overset{K_{\mathrm{os}}}{\rightleftharpoons} \underset{\mathrm{II}}{\mathrm{(H_2O)_5Ni(H_2O)L\text{-}L}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{III}}{\mathrm{(H_2O)_5Ni\text{-}L\text{-}L}} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathrm{IV}}{\mathrm{(H_2O)_4Ni}\Big(\begin{matrix}\mathrm{L}\\ \mathrm{L}\end{matrix}\Big)} + \mathrm{2H_2O}$$

Scheme 2.

In this scheme, I refers to the free ion, II the outer-sphere complex, III the monodentate complex, and IV the bidentate chelate complex, and K_{os} and k represent the outer-sphere complex formation constant and the rate constants of the respective steps.

It is reasonable to assume that the outer-sphere complex formation from the free ions is very rapid compared with the other steps because of its nature of an ion association process, and that the monodentate complex is in a steady state because an observed relaxation is characterized by a single relaxation time. Then, the observed rate constants for the complexation reaction are related to the outer-sphere complex formation constant and the rate constants of each step in Scheme 2 by

$$k_{\mathrm{f}} = K_{\mathrm{os}}k_1\left(\frac{k_2}{k_2+k_{-1}}\right) \tag{3}$$

and

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right). \tag{4}$$

Two limiting cases can be distinguished, depending on the ratio of k_2/k_{-1}. If the first bond formation step (II$\rightleftarrows$III) is rate-determining, i.e., $k_2 \gg k_{-1}$, Eq. 3 is reduced to

$$k_f \simeq K_{OS}k_1, \tag{5}$$

whereas, if the chelate-ring closure step (III$\rightleftarrows$IV) is rate determining, i.e., $k_2 \ll k_{-1}$, Eq. 3 is reduced to

$$k_f \simeq K_{OS}K_1k_2, \tag{6}$$

where $K_1=k_1/k_{-1}$. The observed activation volume for these two limiting cases is approximately expressed by

$$\Delta V_f^{\ddagger} = \Delta V_{OS}^{0} + \Delta V_1^{\ddagger} \text{ (for the former case)} \tag{7}$$

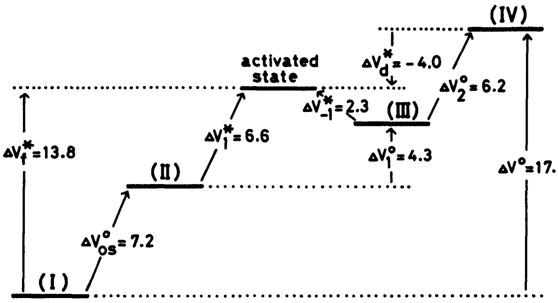
or

$$\Delta V_f^{\ddagger} = \Delta V_{OS}^{0} + \Delta V_1^{0} + \Delta V_2^{\ddagger} \text{ (for the latter case)}, \tag{8}$$

where ΔV_{OS}^{0} is the reaction volume for the outer-sphere complex formation, $\Delta V_1^{\ddagger}$ and ΔV_1^{0} are the activation volume and the reaction volume for the first bond formation after the outer-sphere complex formed, and $\Delta V_2^{\ddagger}$ is the activation volume for the ring-closure after the first bond formed. Thus, experimentally obtained $\Delta V_f^{\ddagger}$ is not a single but a composite term.

It is convenient to separate the outer-sphere complex formation process from the overall reaction. The value of ΔV_{OS}^{0} can be estimated with considerable reliability according to Hemmes[14] as described in a previous paper.[2,3] The values of $\Delta V_f^{\ddagger}-\Delta V_{OS}^{0}$ for some carboxylate ligands are listed in Table 2. Those values for nickel(II) malate and nickel(II) tartrate obtained in the present study are regarded as essentially the same as that for nickel(II) succinate taking into account the error range. This leads to the conclusion that the rate-determining step for the complexation reaction of nickel(II) malate and nickel(II) tartrate is the first bond formation step, since the chelation step is lacking for nickel(II) succinate as mentioned before. The situation is also the same for nickel(II) malonate and nickel(II) tartronate. On the other hand, larger values of $\Delta V_f^{\ddagger}-\Delta V_{OS}^{0}$ for nickel(II) glycolate and nickel(II) lactate, for which the rate-determining step for the complexation reaction is the ring-closure step,[11,12] can be understood with the help of Eq. 8 as described in a previous paper.[3] Comparing the two classes of ligands, glycolate and lactate, and malate and tartrate, both of them form chelate complexes with nickel(II) coordinated by carboxyl and hydroxyl oxygens, but the size of chelate ring is different as mentioned before; the former class forms five-membered ring, whereas the latter forms six-membered ring. The difference in rate-determining step for these two classes of ligands may be attributed to the difference in the chelate-ring size. It is likely that a five-membered ring is imposed to take a sterically distorted structure, and hence, the ring closure becomes rate-determining for five-membered chelate formation.

(a) nickel(II) malate



(b) nickel(II) tartrate

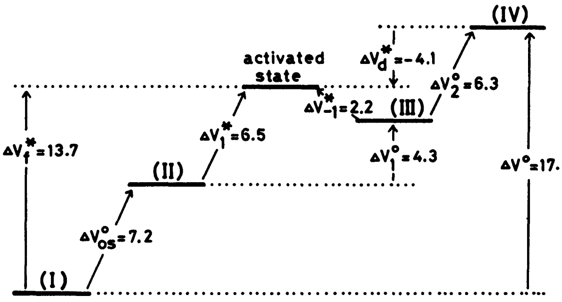


Fig. 2. Volume profile diagrams for the complexation reaction of nickel(II) malate (a) and nickel(II) tartrate (b). I, II, III, and IV in the figure correspond to the species in Scheme 2. The values of volume change in $\mathrm{cm^3\,mol^{-1}}$ are shown in the figure.

It is worth noting that the values of $\Delta V_f^{\ddagger}-\Delta V_{OS}^{0}$ $(=\Delta V_1^{\ddagger})$ obtained for the complexation reaction for which the first bond formation is rate determining are very close to the activation volume of the water exchange of the aquanickel(II) ion, $\Delta V_{H_2O}^{\ddagger}=7.2\pm0.3$ $\mathrm{cm^3\,mol^{-1}}$.[15] This suggests that the activated state for the first bond formation process is the same as that for the water exchange process, and is in accordance with the general picture drawn for the complexation reaction of labil metal ions.[13]

The volume profile diagrams obtained for the complexation reaction of nickel(II) malate and nickel(II) tartrate are shown in Fig. 2. The value of ΔV_1^{0} representing the volume difference between II and III in Scheme 2 was estimated as $\Delta V^{0}-\Delta V_{OS}^{0}$ for nickel(II) succinate, based on the consideration that ΔV_1^{0}, the volume change associated with the first coordination-bond formation by a carboxyl group after the outer-sphere complex formed, is the same at different carboxylic acid. An initial volume increase occurs due to the release of electrostriction on forming the outer-sphere complex (II). It is followed by a volume increase due to the loosening of the water-nickel(II) bond to attain an activated state. Then, a volume decrease occurs on going from the activated state to the monodentate complex (III) due to the completion of the first coordination-bond formation. It is again followed by a volume increase due to the second coordination-bond formation to lead a final chelate complex (IV). The remarkable feature of the volume profile for the complexation with malate and tartrate compared with those obtained previously with malonate and tartronate is that $\Delta V_{\mathrm{d}}^{*}$ is negative for the former ligands, whereas $\Delta V_{\mathrm{d}}^{*}$ for the latter ligands is positive. This difference can be partly attributed to the difference in the bond length of the second coordination bond; for nickel(II) malate and nickel(II) tartrate, the bond length between hydroxyl oxygen and metal ion may be longer and the final complex (IV) has a larger volume, which in turn results in the negative $\Delta V_{\mathrm{d}}^{*}$.

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