release of the electrostriction due to charge neutralization. Equation 18 has been frequently used to estimate the value of $\Delta V_{\rm os}^\circ$.[14] For the present systems, $\Delta V_{\rm os}^\circ$ was calculated to be 6.8 $\mathrm{cm^3\,mol^{-1}}$ from eq 18 by assuming $a = 5$ Å and by using $(\partial \ln \epsilon/\partial P)_T = 59 \times 10^{-6}$[33] $\mathrm{kg^{-1}\,cm^2}$ (see ref 14). Hence, the values of ΔV_1^* are estimated to be 7.3 ± 0.8 $\mathrm{cm^3\,mol^{-1}}$ for nickel(II) succinate and 6.7 ± 0.6 $\mathrm{cm^3\,mol^{-1}}$ for nickel(II) maleate. These values show a close resemblance to the activation volume of the water exchange of the aquonickel(II) ion, $\Delta V_{\rm H_2O}^* = 7.2 \pm 0.3\ \mathrm{cm^3\,mol^{-1}}$, obtained from a high-pressure NMR study.[34] This fact indicates that the rate-determining step is the loss of water from the inner coordination shell of the nickel(II) ion and provides further support for the validity of the Eigen mechanism in the present systems.

Acknowledgment. This work was supported financially in part by the Central Research Institute of Fukuoka University.

Registry No. Nickel, 7440-02-0; succinic acid, 110-15-6; maleic acid, 110-16-7.

---

(32) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, 80, 5059.

(33) Owen, B. B.; Brinkley, S. R. *Chem. Rev.* **1941**, 29, 461.

(34) Ducommun, Y.; Earl, W.; Merbach, A. E. *Inorg. Chem.* **1979**, 18, 2754. Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Ibid.* **1980**, *19*, 3696.

Contribution from the Department of Chemistry,
Faculty of Science, Fukuoka University, Nanakuma, Fukuoka 814-01, Japan

Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. 2. Nickel(II) Glycolate and Nickel(II) Lactate

TOHRU INOUE,* KAZUHIRO SUGAHARA, KIYOTAKA KOJIMA, and RYOSUKE SHIMOZAWA

Received March 25, 1983

Kinetic and equilibrium measurements were carried out for the complexation reactions of nickel(II) glycolate and nickel(II) lactate in water at pressures up to 1000 kg $\mathrm{cm^{-2}}$. The reaction volume, ΔV°, and the activation volume, ΔV_f^*, for the complexation reaction were estimated from the pressure dependence of the stability constant and the rate constant as follows: $\Delta V^\circ = 17.3 \pm 1.0\ \mathrm{cm^3\,mol^{-1}}$ and $\Delta V_f^* = 14.7 \pm 0.5\ \mathrm{cm^3\,mol^{-1}}$ for nickel(II) glycolate; $\Delta V^\circ = 17.6 \pm 0.9\ \mathrm{cm^3\,mol^{-1}}$ and $\Delta V_f^* = 13.5 \pm 0.4\ \mathrm{cm^3\,mol^{-1}}$ for nickel(II) lactate. After correction for the volume change associated with the outer-sphere complex formation ($\Delta V_{\rm os}^\circ = 3.1\ \mathrm{cm^3\,mol^{-1}}$), these activation volumes were consistent with the mechanism previously proposed by Yasunaga et al., where the rate-determining step was assigned to the chelate-ring-closure step. Furthermore, with the aid of the reaction volume for the monodentate complex with succinic acid, the volume profiles for the complexation reaction were obtained, on which some discussions were given.

Introduction

It has been well recognized that the activation volume is a useful parameter for the elucidation of reaction mechanisms.[1] Recently, various apparatus capable of measuring rapid reaction at high pressure have been designed[2–7] and applied to the complexation reactions of labile metal ions.[2,7–9] We have been studying the kinetics and equilibrium of the complex formation between nickel(II) and a variety of carboxylate ligands under high pressure. In a previous paper,[10] we have reported the results obtained with nickel(II) succinate and nickel(II) maleate. The present paper is concerned with the kinetics and equilibrium of nickel(II) glycolate and nickel(II) lactate complexation at various pressures up to 1000 kg $\mathrm{cm^{-2}}$. Kinetics for the same systems at atmospheric pressure have already been studied by Yasunaga et al.,[11,12] and they assigned the rate-determining step of the overall complexation reaction to the chelate-ring closure through the hydroxyl group. The purpose of the present work is to obtain the volume profile for these reactions in order to elucidate the detaile of the reaction mechanism in terms of the volume change.

Experimental Section

Stock solutions of nickel(II) glycolate and nickel(II) lactate were prepared by mixing $\mathrm{NiSO_4}$ and the respective acid in the molar ratio of 1:2, where the sulfate ion was precipitated out as $\mathrm{BaSO_4}$ by adding an equivalent amount of $\mathrm{Ba(OH)_2}$ solution. The concentrations of nickel(II) glycolate and nickel(II) lactate were determined by EDTA titration. Each sample solution was prepared by diluting the stock solution to the desired concentration. All the reagents except glycolic acid were of a guaranteed grade and were used without further purification. Glycolic acid was purified by recrystallization from acetone. The pH of the solution ranged from 5.9 to 6.1 and from 5.9 to 6.0 for nickel(II) glycolate and nickel(II) lactate, respectively. In these pH ranges, most of the ligands are in the dissociated form.

Stability constants of the complexes were determined from conductivity measurements using the same apparatus as described in a previous paper.[10] Kinetic measurements were made by means of a high-pressure *P*-jump technique, which was described in some detail previously.[7,10] Figure 1 shows typical relaxation effects observed in

---

(1) (a) Whalley, E. *Adv. Phys. Org. Chem.* **1964**, *2*, 93. (b) Weale, K. E. "Chemical Reactions at High Pressures"; E. & F. N. Spon Ltd.: London, 1967.

(2) Caldin, E. F.; Grant, M. W.; Hasinoff, B. B. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2247.

(3) Sasaki, M.; Amita, F.; Osugi, J. *Rev. Sci. Instrum.* **1979**, *50*, 1104.

(4) Ishihara, K.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231.

(5) Heremans, K.; Ceuterick, F.; Rijkenberg, J. *Rev. Sci. Instrum.* **1980**, *51*, 252.

(6) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131. Doss, R.; van Eldik, R.; Kelm, H. *Rev. Sci. Instrum.* **1982**, *53*, 1592.

(7) Inoue, T.; Kojima, K.; Shimozawa, R. *Chem. Lett.* **1981**, 259.

(8) (a) Grant, M. W. *J. Chem. Soc., Faraday Trans. 1* **1973**, 69, 560. (b) Grant, M. W.; Wilson, C. J. *Ibid.* **1976**, *72*, 1362. (c) Hasinoff, B. B. *Can. J. Chem.* **1974**, *52*, 910. (d) Hasinoff, B. B. *Ibid.* **1976**, *54*, 1820.

(9) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1981**, *20*, 51. Funahashi, S.; Inamo, M.; Ishihara, K.; Tanaka, M. *Ibid.* **1982**, *21*, 447.

(10) Inoue, T.; Kojima, K.; Shimozawa, R. *Inorg. Chem.*, preceding paper in this issue.

(11) Harada, S.; Okuue, Y.; Kan, H.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 769.

(12) Harada, S.; Tanabe, H.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3125.

0020-1669/83/1322-3977$01.50/0

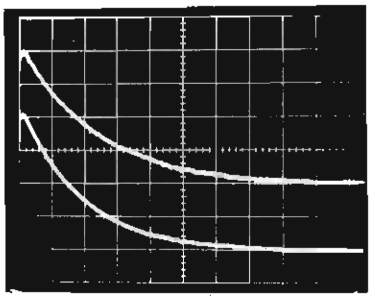


Figure 1. Typical relaxation effects observed in nickel(II) glycolate solution at 20 °C and a final pressure of 1 kg cm^{-2} (lower curve) and 1000 kg cm^{-2} (upper curve). The concentration of nickel(II) glycolate is 6.06×10^{-3} mol dm^{-3}. Time scale is 2 ms/division.

nickel(II) glycolate solution at pressures of 1 and 1000 kg cm^{-2}. These curves represent the time course of conductivity change after pressure perturbation was applied to the system at initial equilibrium. The relaxation time, τ, was determined from the relaxation curve by fitting $Y = A \exp(-t/\tau) + B$ by using a nonlinear least-squares method. All the measurements were carried out at a temperature of 20.0 ± 0.1 °C and pressures of 1, 200, 400, 600, 800, and 1000 kg cm^{-2}.

Results

Equilibrium Study. Stability constants of nickel(II) glycolate and nickel(II) lactate were determined from the conductivity data. The Fuoss–Kraus method, which was applied in a previous work to nickel(II) succinate and nickel(II) maleate systems,[10] cannot be used for unsymmetrical electrolyte systems as in the present case. The method described by Evans and Monk[13] was applied to the determination of the stability constants of the present systems.

The complex formation equilibrium under consideration is written as Scheme I, where L^- respresents the glycolate or lactate ion.

Scheme I

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

The thermodynamic stability constant, K, is expressed by

$$K = \left(\frac{\alpha}{c(1-\alpha)(2-\alpha)}\right)\left(\frac{\gamma_{NiL}}{\gamma_{Ni}\gamma_L}\right) \qquad (1)$$

where c is the analytical concentration of NiL_2, α the fraction of the complex form, and γ the activity coefficient of the respective species. Thus, K is determined according to eq 1 with the knowledge of α.

α was estimated from the conductivity data by the following procedure. The equivalent conductivity of the relevant solution, Λ, is expressed in terms of α, and the ionic equivalent conductivity of respective species, λ, as

$$\begin{aligned}\Lambda &= \lambda_{Ni}(1-\alpha) + \lambda_L(2-\alpha)/2 + \lambda_{NiL}\alpha/2 \\ &= \Lambda_1(1-\alpha) + \Lambda_2\alpha/2 \qquad (2)\end{aligned}$$

where $\Lambda_1 = \lambda_{Ni} + \lambda_L$ and $\Lambda_2 = \lambda_{NiL} + \lambda_L$. From eq 2, α is given by

$$\alpha = \frac{\Lambda_1 - \Lambda}{\Lambda_1 - \Lambda_2/2} \qquad (3)$$

Λ_1 and Λ_2 in eq 3 can be calculated from the corresponding Onsager equations:

$$\Lambda_1 = \Lambda_1{}^\circ - b_1(\mu^{1/2}) \qquad \Lambda_2 = \Lambda_2{}^\circ - b_2(\mu^{1/2}) \qquad (4)$$

Table I. Values of Λ, α, and K of Nickel(II) Glycolate as a Function of NiL_2 Concentration at 20 °C

$c^a/10^{-3}$ mol dm^{-3}	$P = 1$ kg cm^{-2}			$P = 1000$ kg cm^{-2}		
	Λ	α	K^b	Λ	α	K^b
1.23	64.51	0.262	217	69.26	0.163	108.0
1.60	62.36	0.292	204	67.89	0.175	94.4
2.46	57.68	0.366	206	63.18	0.245	103.9
2.66	57.15	0.372	198	63.22	0.237	93.0
2.76	56.03	0.394	214	62.11	0.259	102.8
3.28	53.94	0.429	218	60.09	0.289	105.3
3.31	54.19	0.422	210	60.44	0.281	99.9
3.73	53.13	0.437	204	59.24	0.297	98.9
4.10	51.90	0.457	208	58.45	0.305	96.1
4.26	51.25	0.469	213	57.45	0.325	103.0
4.41	50.92	0.474	212	57.24	0.326	101.0
4.92	49.75	0.492	211	56.51	0.332	95.4
5.32	48.83	0.506	212	55.18	0.355	100.6
			av 210			av 100

[a] Analytical concentration as NiL_2 under atmospheric pressure. [b] In mol^{-1} dm^3.

Table II. Stability Constants, K,[a] as a Function of Pressure at 20 °C and $\mu \rightarrow 0$

	P/kg cm^{-2}					
	1	200	400	600	800	1000
nickel(II) glycolate	210 (6)	174 (6)	146 (6)	126 (5)	112 (5)	100 (5)
nickel(II) lactate	154 (7)	126 (5)	107 (4)	92 (4)	81 (4)	72 (3)

[a] In mol^{-1} dm^3. Standard deviations estimated from the values obtained at 13 different concentrations are shown in parentheses.

where $\Lambda_1{}^\circ$ and $\Lambda_2{}^\circ$ are the equivalent conductivities at infinite dilution, b_1 and b_2 are Onsager's theoretical coefficients that are constant under a given experimental condition,[14] and μ is the ionic strength of the solution. The values of $\Lambda_1{}^\circ$ and $\Lambda_2{}^\circ$ for nickel(II) glycolate and nickel(II) lactate at 25 °C are given in the literature.[13] For application to the present case, these values were corrected for temperature by assuming that Λ° is inversely proportional to the viscosity of the medium. The ionic strength is expressed in terms of c and α by

$$\mu = c(3 - 2\alpha) \qquad (5)$$

Thus, μ is calculated from eq 5 by using an appropriate initial value of α, from which Λ_1 and Λ_2 are calculated by eq 4. Then, the second approximate value of α is obtained from eq 3 with the observed value of Λ, which is used for the next calculation. This procedure was repeated until the value of α converged within 1%. Using the final value of α and the relevant activity coefficients calculated by the Debye–Hückel equation, stability constants were obtained from eq 1. For the determination of K under high pressure, the pressure corrections were made for the viscosity,[15] the dielectric constant,[16] and the density[17] of water, which are necessary for the calculation of the Onsager parameters and the activity coefficient. The density data[17] were also used to correct the concentration in molarity.

Table I lists examples of the values of Λ, α, and K obtained for nickel(II) glycolate at pressures of 1 and 1000 kg cm^{-2}. At the measured concentration range, almost constant values of K were obtained. Stability constants thus obtained at various pressures are summarized in Table II. The present value of K for nickel(II) lactate at 1 kg cm^{-2} is comparable to that in literature[13] ($K = 164$ mol^{-1} dm^3 at 25 °C and $\mu \rightarrow 0$), while for nickel(II) glycolate the value of K obtained is somewhat larger than that in literature[13] ($K = 183$ mol^{-1} dm^3 at 25 °C and $\mu \rightarrow 0$).

---

(13) Evans, W. P.; Monk, C. B. *J. Chem. Soc.* **1954**, 550.

(14) Bockris, J. O.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1973; Chapter 4.

(15) Horne, R. A.; Johnson, D. S. *J. Phys. Chem.* **1966**, *70*, 2182.

(16) Srinivasan, K. R.; Kay, R. L. *J. Chem. Phys.* **1974**, *60*, 3645.

(17) Bridgman, P. W. "The Physics of High Pressure", G. Bell: London, 1949.

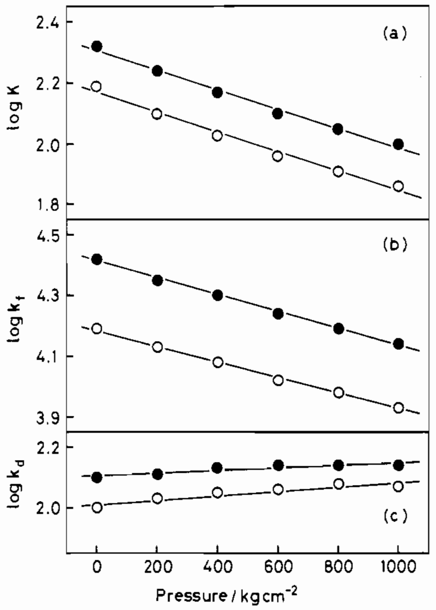


Figure 2. Pressure dependence of (a) log K, (b) log k_f, and (c) log k_d at 20 °C: ●, nickel(II) glycolate; ○, nickel(II) lactate. Solid lines show the linear least-squares fits to the data points.

From the pressure dependence of the stability constants, the reaction volume for the complex formation, ΔV°, can be estimated according to the relation[1b]

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta V^\circ - RT\kappa_0 \qquad (6)$$

where κ_0 represents the solution compressibility. In eq 6, $-RT\kappa_0$ is the correction term for the compression required when the molarity scale of concentration is used and has the value of 1.1 cm^3 mol^{-1} for the present case. Figure 2a shows a plot of log K against pressure. From the slope of the fitted straight line and from eq 6, the reaction volumes were estimated to be as follows: $\Delta V^\circ = 17.3 \pm 1.0$ cm^3 mol^{-1} for nickel(II) glycolate; $\Delta V^\circ = 17.6 \pm 0.9$ cm^3 mol^{-1} for nickel(II) lactate.

Kinetic Study. The rate constants for the complex-formation reaction were determined from the p-jump relaxation data. For the reaction as represented by Scheme I, the reciprocal relaxation time is given by the expression

$$1/\tau = k_f\gamma_{Ni}\gamma_L(c_{Ni} + c_L) + k_d\gamma_{NiL} \qquad (7)$$

where k_f and k_d are the rate constants of the complex formation and the dissociation at zero ionic strength and c_{Ni} and c_L are the equilibrium concentrations of the nickel(II) and ligand ions. On the assumption that $\gamma_L = \gamma_{NiL}$ and with use of the independently determined stability constant, eq 7 is converted to

$$1/(\tau\gamma_{NiL}) = k_f[\gamma_{Ni}(c_{Ni} + c_L) + 1/K] \qquad (8)$$

The values of k_f were determined from the relaxation times according to eq 8. The equilibrium concentrations and the activity coefficients in eq 8 were calculated from the stability constants by using an iteration procedure, where the Davies equation[18] was applied to the calculation of the activity coefficients. Necessary pressure corrections were also made for the case under high pressure as in an equilibrium study. Some examples of the results are shown in Table III. The dissociation rate constants of the complex were determined from the relation

$$k_d = k_f/K \qquad (9)$$

Table III. Relaxation Times and Rate Constants for Complex Formation at 20 °C

	$P = 1$ kg cm^{-2}		$P = 1000$ kg cm^{-2}	
$c^a/10^{-3}$ mol dm^{-3}	$1/\tau$/ s^{-1}	$k_f/10^4$ mol^{-1} dm^3 s^{-1}	$1/\tau$/ s^{-1}	$k_f/10^4$ mol^{-1} dm^3 s^{-1}
		Nickel(II) Glycolate		
3.99	239	2.55	193	1.29
5.99	268	2.49	219	1.31
7.99	305	2.55	240	1.33
12.0	368	2.64	278	1.36
16.0	422	2.71	317	1.42
22.0			340	1.37
28.0	506	2.60	398	1.47
33.9	577	2.73	408	1.41
39.9	628	2.78	436	1.42
49.9	690	2.79	490	1.47
		av 2.65		av 1.39
		Nickel(II) Lactate		
1.58	147	1.66	136	0.846
3.16	170	1.62	148	0.826
4.74	177	1.50	164	0.845
6.32	196	1.52		
11.1	230	1.48	196	0.822
14.2	267	1.58	219	0.859
17.4	268	1.47	233	0.863
22.1	294	1.48	254	0.876
26.8	336	1.58	282	0.917
31.6	356	1.57	268	0.828
		av 1.54		av 0.854

[a] Analytical concentration under atmospheric pressure.

Table IV. Rate Constants for the Complex Formation Reaction of Nickel(II) Glycolate and Nickel(II) Lactate as a Function of Pressure at 20 °C and $\mu \to 0^a$

	nickel(II) glycolate		nickel(II) lactate	
P/kg cm^{-2}	$k_f/10^4$ mol^{-1} dm^3 s^{-1}	$k_d/10^2$ s^{-1}	$k_f/10^4$ mol^{-1} dm^3 s^{-1}	$k_d/10^2$ s^{-1}
1	2.65 (0.11)	1.26 (0.06)	1.54 (0.06)	1.01 (0.06)
200	2.24 (0.08)	1.29 (0.07)	1.35 (0.04)	1.07 (0.05)
400	1.99 (0.06)	1.36 (0.07)	1.20 (0.05)	1.12 (0.06)
600	1.75 (0.06)	1.39 (0.07)	1.05 (0.04)	1.14 (0.06)
800	1.55 (0.04)	1.39 (0.07)	0.96 (0.04)	1.19 (0.07)
1000	1.39 (0.06)	1.38 (0.09)	0.85 (0.03)	1.18 (0.06)

[a] Standard deviations estimated from the values obtained at 9–12 different concentrations are shown in parentheses.

The rate constants thus obtained are summarized in Table IV.

From the pressure dependence of the rate constants, the activation volume of the reaction can be estimated according to a relation analogous to eq 6.[1] Parts b and c of figure 2 show plots of log k_f and log k_d against pressure. In the measured pressure range, a linear relationship was obtained between the logarithm of the rate constant and 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 to be as follows: $\Delta V_f^* = 14.7 \pm 0.5$ cm^3 mol^{-1} and $\Delta V_d^* = -2.6 \pm 0.7$ cm^3 mol^{-1} for nickel(II) glycolate; $\Delta V_f^* = 13.5 \pm 0.4$ cm^3 mol^{-1} and $\Delta V_d^* = -4.1 \pm 0.6$ cm^3 mol^{-1} for nickel(II) lactate.

Discussion

The metal complexation reaction is generally understood in terms of the stepwise mechanism postulated by Eigen.[19,20] For the nickel(II) glycolate and nickel(II) lactate systems where bidentate chelate complexes are formed, this mechanism may be represented by Scheme II.[20] where I is the free ion,

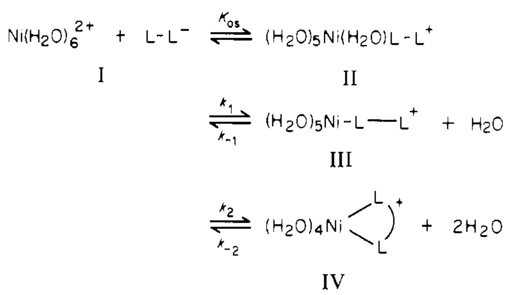
---

(18) Davies, C. W. *J. Chem. Soc.* **1938**, 2093.

(19) Eigen, M.; Wilkins, R. G. "Mechanisms of Inorganic Reactions"; American Chemical Society: Washington, DC, 1965; Adv. Chem. Ser. No. 49.

(20) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408.

Scheme II



II is the outer-sphere complex, III is the monodentate complex with one end of the ligand left free, IV is the bidentate chelate complex, K_{os} is the outer-sphere complex formation constant, and k's are the rate constants of each step. Under the reasonable assumptions that the outer-sphere complex formation from the free ions is very rapid compared with other steps and that the monodentate complex is in a steady state, the overall rate constants are related to the rate constants of each step in Scheme II by the equations

$$k_f = K_{os}k_1\left(\frac{k_2}{k_2 + k_{-1}}\right) \qquad (10)$$

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2 + k_{-1}}\right) \qquad (11)$$

According to Yasunaga et al.[11,12] the rate-determining step of the nickel(II) glycolate and nickel(II) lactate complexation reactions is considered to be the chelate-ring-closure step. This assignment is supported from the present results regarding the volume change associated with the complexation reaction as is shown below.

If the formation of the monodentate species is rate determining, i.e., $k_{-1} << k_2$, eq 10 can be reduced to

$$k_f \simeq K_{os}k_1 \qquad (12)$$

Then, the experimentally obtained overall activation volume, ΔV_f^*, is expressed by

$$\Delta V_f^* = \Delta V_{os}° + \Delta V_1^* \qquad (13)$$

where $\Delta V_{os}°$ represents the reaction volume for the outer-sphere complex formation and ΔV_1^* the activation volume for the first bond formation. The value of $\Delta V_{os}°$ can be estimated from the Hemmes equation[21]

$$\Delta V_{os}° = RT\left[\frac{|z_+z_-|e^2}{a\epsilon kt}\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T - \kappa_0\right] \qquad (14)$$

where z_+e and z_-e are the charges on the metal and ligand ions, a is the distance of closest approach of the two ions, ϵ is the dielectric constant of the medium, and other symbols have their usual meanings. According to eq 14, $\Delta V_{os}°$ is calculated to be 3.1 cm^3 mol^{-1} for the present case ($|z_+z_-| = 2$) at 20 °C by using the appropriate values of the parameters.[8a] Then, ΔV_1^* is estimated to be 11.6 cm^3 mol^{-1} for nickel(II) glycolate and 10.4 cm^3 mol^{-1} for nickel(II) lactate. On the other hand, it is well established that in a monodentate complex formation the water loss from the inner coordination shell of the metal ion is rate determining. The activation volume of the water exchange of the aquonickel(II) ion has been estimated to be 7.2 ± 0.3 cm^3 mol^{-1} on the basis of a high-pressure NMR study.[22] In fact, thus far, activation volumes close to 7 cm^3 mol^{-1} have been obtained for several monodentate complexes[2,10] and bidentate complexes[2,8a] with the rate-determining step that of the first bond formation. The ΔV_1^* values estimated above are much larger than that expected for a water-loss process, and hence it is concluded that the rate-determining step is not the first bond formation but the other step, chelate-ring closure.

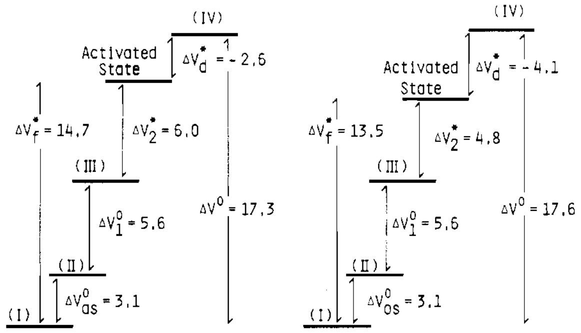


Figure 3. Volume profiles for the complex-formation reaction of nickel(II) glycolate (left) and nickel(II) lactate (right). I, II, III, and IV correspond to the compounds in Scheme II. The values of volume change in cm^3 mol^{-1} are shown in the figure. For the estimation of $\Delta V_{os}°$ and $\Delta V_1°$, see text.

When chelate-ring closure is rate determining, i.e., $k_{-1} >> k_2$, eq 10 and 11 are simplified to

$$k_f \simeq K_{os}K_1k_2 \qquad k_d \simeq k_{-2} \qquad (15)$$

where $K_1 = k_1/k_{-1}$. In this case, ΔV_f^* is approximately expressed by

$$\Delta V_f^* = \Delta V_{os}° + \Delta V_1° + \Delta V_2^* \qquad (16)$$

where $\Delta V_1°$ represents the reaction volume for the formation of the monodentate species from the outer-sphere complex and ΔV_2^* the activation volume for the ring-closure step. For nickel(II) glycolate and nickel(II) lactate, it may be considered that the first bond is formed between the nickel(II) ion and the carboxyl group rather than the hydroxyl group. Then, $\Delta V_1°$ corresponds to the volume change associated with the coordination bond formation by a carboxyl group after the outer-sphere complex formed. The $\Delta V_1°$ value may be estimated from the reaction volume and $\Delta V_{os}°$ for nickel(II) succinate, which is considered to form a monodentate complex coordinated by a single carboxyl group; $\Delta V° = 11.1 \pm 0.9$ cm^3 mol^{-1} and $\Delta V_{os}° = 6.8$ cm^3 mol^{-1},[10] which indicates that a volume increase of about 4.3 cm^3 mol^{-1} results from the bond formation. The positive $\Delta V_1°$ may be ascribed to the elimination of solvated water around the coordinating group due to the bond formation, which produces the free water and resultant volume increase. Then, in estimating $\Delta V_1°$ from the $\Delta V°$ value of nickel(II) succinate, it should be taken into account that the outer-sphere complex has different electric charge in the two cases, i.e., charges are neutralized in nickel(II) succinate, while a unit positive charge remains in nickel(II) glycolate and nickel(II) lactate systems. Hence, in the latter cases, the hydrated water around the coordinating group may be affected by the electrostriction, and the volume change accompanied by the transfer of the hydrated water to the free water may be somewhat larger than that estimated from $\Delta V° - \Delta V_{os}°$ for nickel(II) succinate. The approximate value of this excess volume change may be estimated according to the calculation of Whalley.[1a] He showed that the volume of water is reduced by 1.3 cm^3 mol^{-1} by the electrostriction caused by a unit charge. This calculation was made on the basis of the pressure derivative of the Gibbs energy change due to electrostatic interaction when a point charge is transferred from a medium of unit dielectric constant to the solvent and is only approximate; however, the obtained value may be used as a crude estimate of the excess volume change resulting

---

(21) Hemmes, P. *J. Phys. Chem.* **1972**, *76*, 895.

(22) Ducommun, Y.; Earl, W.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2754. Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Ibid.* **1980**, *19*, 3696.

from the effect of the electrostriction. Hence, $\Delta V_1{}^\circ$ values is estimated to be about 5.6 cm^3 mol^{-1} for the present systems.

Volume profiles for the complexation reactions of nickel(II) glycolate and nickel(II) lactate are shown in Figure 3 where $\Delta V_{os}{}^\circ$ and $\Delta V_1{}^\circ$ were derived as described above. As is seen from this figure, almost similar features were obtained for both systems; the difference in the structures of glycolic acid and lactic acid is only the methyl group on the α-carbon. The volume change associated with chelation by the hydroxyl group is estimated to be about 9 cm^3 mol^{-1}, which is larger than $\Delta V_1{}^\circ$ by about 3 cm^3 mol^{-1}. This difference in the volume change may be ascribed partly to the fact that the interaction between nickel(II) and the hydroxyl oxygen is weak and the bond length is longer than that between nickel(II) and the carboxyl oxygen and partly to the increase in free volume accompanied by the formation of ring structure, which is too small to be occupied by the solvent molecule.[1] At the present time, these two contributions can not be estimated separately. If the latter contribution is neglected tentatively, it is shown by the calculation using the van der Waals radii of oxygen that the difference in the volume change by 3 cm^3 mol^{-1} corresponds to the difference in the bond length by about 0.8 Å.

The activated state of the overall complexation reaction is in the course of the chelation process and may be considered to be the state where the bond between nickel(II) and the hydroxyl oxygen is partly formed. The positive activation volume may be attributed to the two factors: (i) The bond length between nickel(II) and the hydroxyl oxygen at an activated state is longer than that between the metal and water at an initial state (III) (i.e., "structural" term). (ii) The hydrated water around the hydroxyl group is partly eliminated to form the free water in order to attain the activated state (i.e., "solvation" term). It is impossible to separate the present $\Delta V_2{}^*$ into the two terms. However, it may be considered qualitatively that the contribution from the solvation term is more significant for the chelation process, because, if otherwise, the formation of the final stable chelate (IV) from the activated state should accompany the negative volume change. A slight difference in $\Delta V_2{}^*$ for nickel(II) glycolate and nickel(II) lactate might be regarded as reflecting the difference in the bond length between nickel(II) and the hydroxyl oxygen at an activated state, which may be reflected to $\Delta V_2{}^*$ through the bond length itself and the degree of desolvation. However, more detailed discussion on this report is not given at the present time.

Acknowledgment. This work was supported financially in part by the Central Research Institute of Fukuoka University.

Registry No. Nickel, 7440-02-0; glycolic acid, 79-14-1; lactic acid, 50-21-5.

Contribution from the Department of Inorganic Chemistry,
The Royal Institute of Technology, S-100 44 Stockholm, Sweden

Studies of Metal Carbonate Equilibria. 8. Structure of the Hexakis(carbonato)tris[dioxouranate(VI)] Ion in Aqueous Solution. An X-ray Diffraction and ^{13}C NMR Study

MÄRTHA ÅBERG,* DIEGO FERRI, JULIUS GLASER, and INGMAR GRENTHE

Received February 28, 1983

The X-ray scattering from moderately concentrated dioxouranium(VI) carbonate solutions with the major part of uranium bound in the trinuclear complex $(UO_2)_3(CO_3)_6{}^{6-}$ has been measured. A model for the structure of this complex consistent with the scattering data and compatible with ^{13}C NMR data is suggested. The complex is triangular with a U–U distance of 4.946 (5) Å. There are two sets of coordinated carbonate ions, three bridging and three terminal ones. The latter are bonded through two oxygens to uranium. The bridges are formed through bidentate coordination of the carbonate ion to two uranium atoms. The overall symmetry of the complex is close to D_{3h}, and each uranium(VI) has an approximately hexagonal-bipyramidal coordination geometry, similar to those found in e.g. UO_2CO_3(s) and $K_4[UO_2(CO_3)_3]$(s). The ^{13}C NMR chemical shifts for the two types of carbonate ions in the complex have been determined to be 168.7 and 167.3 ppm, respectively, from Me_4Si.

Introduction

The equilibria between $UO_2{}^{2+}$, H_2O, and CO_2(g) at 25 °C in a 3 M $NaClO_4$ medium have been studied at acidities ranging from $[H^+] \simeq 10^{-5}$ M to $[H^+] \simeq 10^{-7}$ M by potentiometric measurements.[1] The data could be explained by assuming the equilibrium

$$3UO_2(CO_3)_3{}^{4-} + 6H^+ \rightleftharpoons (UO_2)_3(CO_3)_6{}^{6-} + 3CO_2(g) + 3H_2O$$

The structure of the mononuclear complex $UO_2(CO_3)_3{}^{4-}$ is well-known from crystal structures.[2-4] There is no reason to believe that the structure in solution is very much different.

The structure of the trinuclear complex $(UO_2)_3(CO_3)_6{}^{6-}$ is unknown. Preliminary ^{13}C NMR data[1] have indicated the presence of two types of coordinated carbonate ions, presumably bridging and terminal ones.

Fairly concentrated solutions, where more than 80% of the total uranium is bound in the trinuclear complex, can be prepared. Hence, it seems likely that X-ray investigations can give information on the structure of the complex in solution.

Experimental Section

Materials and Analysis. Dioxouranium(VI) (uranyl) perchlorate solutions, perchloric acid, sodium hydrogen carbonate, and sodium perchlorate were prepared and analyzed as described elsewhere.[1]

Uranyl nitrate solutions were prepared from $UO_2(NO_3)_2(H_2O)_6$ (Merck, reagent grade) without further purification. They were

---

[1] Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F. *Inorg. Chem.* **1981**, *20*, 463.

[2] Graziani, R.; Bombieri, G.; Forsellini, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2059.

[3] Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* **1980**, *58*, 1651.

[4] Coda, A.; Della Giusta, A.; Tazzoli, V. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1496.

0020-1669/83/1322-3981$01.50/0