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A HIGH PRESSURE P-JUMP APPARATUS AND ITS APPLICATION TO THE KINETICS OF NICKEL MALONATE COMPLEX FORMATION

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A pressure-jump apparatus capable of following fast reactions at high pressures was constructed. Using this apparatus the activation volume for the reaction of nickel malonate complex formation was successfully determined at 20°C. The results were interpreted in terms of the Eigen-Wilkins mechanism.

The pressure-jump (P-jump) technique is very effective for kinetic investigation of fast reactions in solution. In conventional P-jump experiments the applied pressure is suddenly released to the atmospheric pressure and the relaxation process induced by the abrupt pressure drop was followed by an appropriate detection. From the kinetic measurements at various pressures, one can evaluate an activation volume which is an important information to elucidate the reaction mechanism. However, only a few studies have been reported for the fast reactions, *e.g.*, those reported by Caldin and coworkers for several metal complex formation reactions using high pressure laser T-jump technique.1) In this work, the P-jump apparatus was constructed to follow the pressure-jump induced relaxation under high pressures, and kinetics for complexation reaction of Ni(II) with malonate anion was investigated at various pressures from 1 bar to 980 bar.

The schematic diagram of the pressure-jump system is shown in Fig. 1. The main improvement to meet the high pressure requirement is that a pressure reservoir is installed on the top of brass diaphragm. With cutoff valves open both of the reservoir and cell compartment were pressurized to the desired pressure, P, by a hydraulic pump. Then, cutoff valves were closed, and only the pressure of the cell compartment was further increased by ΔP until the brass diaphragm burst. Thus, the sample cell pressure abruptly dropped from $P+\Delta P$ to P'. The final pressure P' was higher than P since the system was closed. The difference between P and P' may depend on both the volume ratio of the reservoir to cell compartment and the magnitude of ΔP. In the present apparatus, P' was higher by about 30 bar than P for ΔP of about 130 bar as used throughout this work. The final pressure could be controlled within about ± 5 bar. Water was used as the pressurizing fluid.

The concentration changes of species after a pressure drop were detected by usual electroconductivity method at 200 kHz. Just after the rupture of brass diaphragm, the relaxation signal was somewhat disturbed by the overlapping of a high frequency signal probably due to the reflection of a shock wave from the

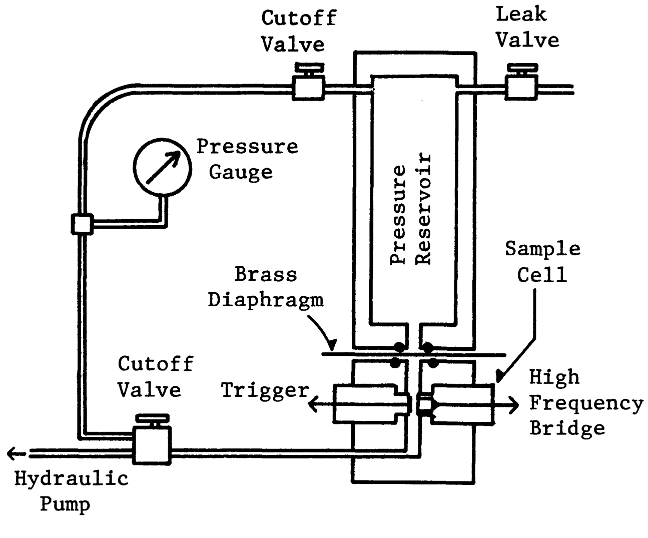

Fig. 1. Schematic diagram of pressure-jump system

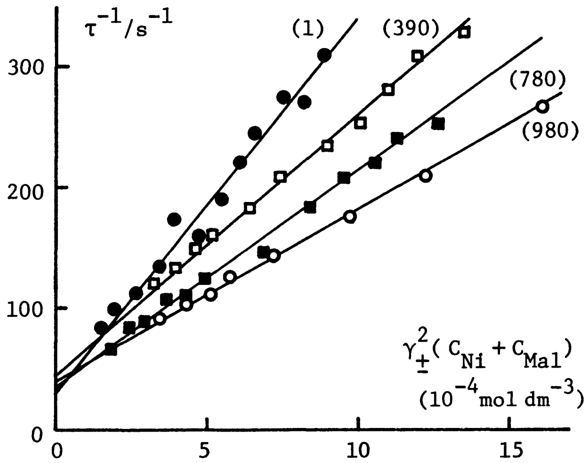

Fig. 2. Plot of τ^{-1} vs. $\gamma_{\pm}^{2}(C_{Ni}+C_{Mal})$ at 20°C. Final pressures (bar) are indicated in parentheses.

pressure reservoir wall. This interference signal, however, decayed within about 4 ms, and did not disturb the present measurements significantly.

Sample solutions of nickel malonate were prepared according to the procedure described in the literature.2) Kinetic measurements were carried out at the various total concentrations of nickel malonate at 20°C and at several pressures. The observed relaxation curve was characterized by a single relaxation time.

The relaxation times were analyzed in terms of the reaction scheme (M^{2+} = metal ion, L^{2-} = ligand, ML = complex) :

$$M^{2+} + L^{2-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} ML \tag{1}$$

which leads to the equation :

$$\tau^{-1} = k_f \gamma_{\pm}^{2} (C_M + C_L) + k_d \tag{2}$$

where τ is the relaxation time, k_f and k_d are the formation and dissociation rate constants, C_M and C_L are equilibrium concentrations of the metal ion and the ligands, and $\gamma_{\pm}$ is the mean activity coefficient of the free ions.

The complex formation constants, K ($=k_f/k_d$), of nickel malonate at high pressures, which are needed for the calculation of C_M and C_L, were not known. Hence, k_f, k_d, and K were determined from the kinetic data by an iterative computer technique. As a first approximation, the value of K at 1 bar was taken to calculate the concentration of free ions under higher pressures. The activity coefficients of the ions were calculated by the Davies equation,3) and the approximate values of k_f and k_d were estimated according to Eq.2 by means of least-squares analysis. Then taking a value of K as given by k_f/k_d, the calculation was cyclically performed until the calculated values of K became constant within 1%. Since the variation of $\gamma_{\pm}$ values in the pressure range studied was within only a few percent, this effect was neglected in the calculation. Concentrations were based on the molarity scale, and no correction for compression of the solvent was made since the differences in the results at 980 bar calculated with and without the correction were much smaller than the experimental errors. The final plots are shown in Fig. 2, and the rate and equilibrium constants obtained are listed in Table 1. The values of these parameters at 1 bar agree with those in the literature.$^{2)}$

The activation volume, ΔV_f^*, for the nickel malonate complex formation was evaluated from the pressure dependence of k_f. A plot of $\log k_f$ against pressure is shown in Fig. 3. From the slope of the straight line best fitted to the plot the value of ΔV_f^* was calculated to be 16.0 ± 2.1 $\mathrm{cm^3 mol^{-1}}$.

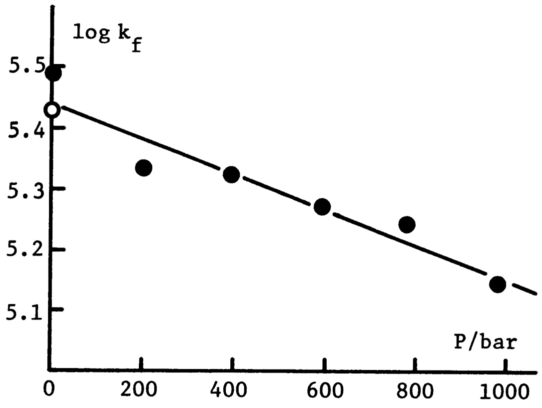

Fig. 3 Plot of $\log k_f$ against pressure.
●; This work, ○; Reference 2

For the metal complex formation reaction, the Eigen-Wilkins mechanism$^{4)}$ has been widely accepted, according to which the formation of the outer-sphere complex is succeeded by the ligand water dissociation from the metal ion in the transition state. This mechanism may be formulated as follows for the present system.

$$\mathrm{Ni(H_2O)_6^{2+} + Mal^{2-}} \underset{}{\overset{K_{os}}{\rightleftharpoons}} \underset{\text{(I)}}{\mathrm{[(H_2O)_5Ni(H_2O)Mal]}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{H_2O} + \underset{\text{(II)}}{\mathrm{[(H_2O)_5NiMal]}}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{(III)}}{\mathrm{[(H_2O)_4NiMal]}} + \mathrm{H_2O} \qquad (3)$$

where (I) is the outer-sphere complex, (II) is the half-bonded intermediate, and (III) is the bidentated complex.

The rate constant k_f in Eq.1 is expressed by Eq.4 under the assumption that the intermediate (II) is in a steady state and that $k_{23} \gg k_{21}$.

$$k_f = K_{os}\, k_{12} \qquad (4)$$

Table 1. Rate Constants and Kinetically Determined Complex Formation Constants for Nickel-Malonate System at 20°C, $\mu \rightarrow 0$.

Pressure/bar	$k_f/10^5\mathrm{mol^{-1}dm^3s^{-1}}$	$k_d/\mathrm{s^{-1}}$	$K/10^3\mathrm{mol^{-1}dm^3}$
1	3.08 ± 0.15 (2.7^a)	32 ± 9 (24^a)	9.6 ± 2.2 (12^a)
200	2.16 ± 0.04	44 ± 3	4.9 ± 0.2
390	2.12 ± 0.04	48 ± 4	4.4 ± 0.3
590	1.87 ± 0.03	34 ± 2	5.5 ± 0.2
780	1.76 ± 0.05	35 ± 4	5.0 ± 0.4
980	1.39 ± 0.03	42 ± 3	3.3 ± 0.1

Errors are standard deviation derived from least-squares analysis.
a) Reference 2.

where K_{os} is the outer-sphere complex formation constant and k_{12} is the first order rate constant for the dissociation of water from (I). From Eq.4 it is apparent that

$$\Delta V^{*}_{f} = \Delta V^{0}_{os} + \Delta V^{*}_{12} \tag{5}$$

where ΔV^{0}_{os} is the reaction volume for the formation of the outer-sphere complex, and ΔV^{*}_{12} is the activation volume for water loss. According to Hemmes,[5)] ΔV^{0}_{os} is given by the expression

$$\Delta V^{0}_{os} = RT[(|z_{+}z_{-}|e^{2}/aDkT)(\partial \ln D/\partial P)_{T} - \beta] \tag{6}$$

where z_{+} and z_{-} are the charges of the two ions, a is the distance of closest approach, D is the dielectric constant, β is the solution compressibility, and other symbols have their usual meanings. This expression has been frequently used to estimate the values of ΔV^{0}_{os}.[1b,1c)] For the nickel malonate complex, ΔV^{0}_{os} was calculated to be 7.3 $cm^{3}mol^{-1}$ from Eq.6 using the appropriate numerical values (see Reference 1b). Hence, the value of ΔV^{*}_{12} is estimated to be 8.7 ± 2.1 $cm^{3}mol^{-1}$. As seen in Table 2, this value is comparable with those reported for other nickel complexes with different ligands. The essential conformity among the values of ΔV^{*}_{12} provides an additional support for the validity of the Eigen-Wilkins mechanism for nickel malonate complex formation.

Table 2. Calculated Values of ΔV^{*}_{12} Assuming the Eigen-Wilkins Mechanism for Nickel Complex Formation Reaction

Ligand	PADA[a]	NH_3[a]	Glycinate[b]	Malonate[c]
$\Delta V^{*}_{12}/cm^{3}mol^{-1}$	7.7 ± 0.3	6.0 ± 0.3	7 ± 1	8.7 ± 2.1

a) Reference 1a. b) Reference 1b. c) This Work.

The reaction volume and the activation volume for the reverse reaction should be determined from the pressure dependence of $\log K$ and $\log k_{d}$. However, the plots of these parameters against pressure considerably scattered because of large errors involved in k_{d} calculated from the intercept in Fig. 2. Thus, the accuracy of the estimation by this procedure was so poor that the analysis of the pressure dependence of K and k_{d} was not given here. It may be required to determine the values of K at each pressure from the independent experiment.

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