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Kinetic Studies of the Nickel Maleate Complex Formation in Solution by the Pressure-jump Method

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Nickel maleate complex formation reaction in an aqueous solution, $Ni^{2+}+Mal^{2-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} NiMal$, where Mal^{2-} represents the maleate ion, was studied by the pressure-jump method. The rate constants and the stability constant were obtained; $k_f=8.4\times10^5\ M^{-1}\ s^{-1}$, $k_d=2.1\times10^3\ s^{-1}$, and $K=4\times10^2\ M^{-1}$ at 25°C and at $\mu\rightarrow0$. The thermodynamic parameters of this reaction were obtained from studies at various temperatures between 10 and 30°C. The results indicate that the nickel maleate is stable as a monodentated complex rather than as a chelate complex. Moreover, the nickel dicarboxylate complex formation reactions and the rate equations were discussed.

Static measurements of the stabilities of the chelate complexes[1-3] have revealed that the stabilities depend greatly on the carbon number or the structure of the ligands; *e. g.*, the five-membered ring complex is more stable than the six membered one. In the nickel dicarboxylate, the oxalate ion makes a more stable complex than that of the malonate.[4] The same ligand effects can also be observed in the kinetic measurements;[5,6] the difference in the stabilities has been attributed to that of the ligand-dissociation rate constants.

The nickel dicarboxylate complex formation reaction, which involves the replacement of the two coordinated water molecules, has usually been interpreted

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[1] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., (1967).

[2] F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **59**, 1203 (1955).

[3] K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **29**, 523 (1967).

[4] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-ion Complexes," Special Publication No. 17, The Chemical Society, London, (1964).

[5] G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

[6] F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).

by the step-by-step mechanism proposed by Eigen *et. al.*[7] For the assignment of the relaxation effects, however, two different theories have been proposed. According to the first theory,[5,6,8,9] the rate-determining step is supposed to be the formation of the first bond between the metal ion and the ligand, whereas in the second theory[10,11] the ring closure of the chelate is assumed.

One of the two purposes of the present work is to discuss these two theories; the other was to ascertain the ligand effects on the stability constants, the rate constants, the reaction mechanisms, and the thermodynamic parameters of the nickel dicarboxylate complex formation reactions.

Experimental

All of the chemicals used were of a reagent grade. A stock solution of the nickel maleate was prepared by mixing a stoichiometric amount of $NiSO_4$ with maleic acid, and the sulfate ion was precipitated out as the insoluble $BaSO_4$. The solid $BaSO_4$ was removed by filtration. The concentration of the nickel maleate of the stock solution was determined by dimethylglyoxime titration. Each solution studied was prepared by diluting the stock solution to the desired concentration. The pH's of the solutions were 7.1—7.2, with most of the ligands in the dissociated form. No buffering or supporting electrolytes were added, and so the ionic strength of the solution was varied arbitrarily.

The pressure-jump apparatus used has been described in considerable detail elsewhere.[8] The only significant change made was that a single cell is now employed, rather than a double cell; *i. e.*, a valuable resistor was used in place of the reference cell. This improvement has resulted not only in making the experiments more easy, but also in increasing the signal-to-noise ratio. The time constant of the apparatus was 100 μs. The solution of either the nickel ion or the maleate ion in the absence of the other showed no relaxation effect in the present time range. This proved that the relaxation effect is due to the nickel maleate complex formation reaction.

The measurements were carried out at 10, 15, 20, 25, and 30°C in the concentration range from 5.06×10^{-4} to 5.06×10^{-2} M of the nickel maleate. The relaxation times quoted are the mean values of several runs.

Results

Table 1. Relaxation times and experimental conditions for nickel maleate system at 25°C

C_0[a] (10^{-4} M)	C_{NiMal} (10^{-4} M)	$C_{Ni}=C_{Mal}$ (10^{-4} M)	μ (10^{-4})	$\gamma_\pm$	$1/\tau$ ($10^3\,s^{-1}$)
5.1	0.8	4.3	17.3	0.84	2.3
8.1	1.7	6.4	25.8	0.81	2.5
10.1	2.4	7.7	30.9	0.79	2.7
20.2	7.0	13.2	52.9	0.74	3.1
30.4	12.6	17.8	71.0	0.71	3.4
40.5	18.8	21.7	86.7	0.69	3.7
50.6	25.4	25.2	100.8	0.68	3.9
60.7	32.3	28.4	113.7	0.66	4.1
81.0	46.8	34.2	136.8	0.64	4.4
101.2	61.9	39.3	157.3	0.63	4.7
202.4	142.7	59.7	238.9	0.58	5.5
303.6	228.1	75.5	302.1	0.55	6.0
404.8	315.9	88.9	355.5	0.53	6.4
506.0	405.3	100.7	402.7	0.51	6.8

a) C_0 refers to the total stoichiometric concentrations of the nickel maleate.

The experimental conditions and the observed relaxation times at 25°C are shown in Table 1. The concentration dependence of the relaxation time can be explained on the basis of this simple mechanism:

$$M^{2+} + L^{2-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} ML. \qquad (1)$$

where M^{2+} is the metal ion, L^{2-} is the ligand, and ML is the complex. For such a mechanism, $1/\tau$ is given by the expression:

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

where k_f, k_d are the rate constants of the complex formation and the dissociation at zero ionic strength respectively, where $\gamma_\pm$ is the mean activity coefficient of the free ions at a finite ionic strength, and where C_M, C_L are the concentrations of the metal and the ligand ions respectively.

For the evaluation of the rate constants, $1/\tau$ is normally plotted against $\gamma_\pm{}^2(C_M+C_L)$. The intercept, corresponding to $\gamma_\pm{}^2(C_M+C_L)=0$, yields k_d, while k_f can be obtained from the slope. Such a plot requires a knowledge of the stability constant, K, in order to calculate the concentrations of the free ions. An appropriate literature value was not, however, available, and so the values were evaluated as follows. As the first approximation, a value of K which was roughly estimated from that of the succinate complex[9] was used to calculated the ionic concentrations. The mean activity coefficients were evaluated from the ionic strengths, which had themselves been calculated from the ionic concentration, using the Kielland equation.[12] Then, the $1/\tau$ values were plotted against $\gamma_\pm{}^2(C_M+C_L)$. The stability constant, which should coincide with the first estimated K value, was obtained from the ratio between k_f and k_d. Successive approximations were performed until a constant K value was obtained. The final results are shown in Fig. 1. The rate and the stability constants at various temperatures are given in Table 2.

The Arrhenius energies of activation, $\Delta E_f^{\neq}$ and $\Delta E_d^{\neq}$, were obtained from the plot of $\log k_f$ and $\log k_d$ respectively against $1/T$, as is shown in Fig. 2. The other thermodynamic parameters of the complex formation, *i. e.*, the entropy of activation, $\Delta S_f^{\neq}$, the enthalpy of activation, $\Delta H_f^{\neq}$, and the free energy of activation, $\Delta G_f^{\neq}$, were calculated from the following

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[7] M. Eigen and L. De Mayer, "Technique of Organic Chemistry," Vol. VIII, 2nd Ed., S. L. Friess, E. S. Lewis and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., Part 2, (1963).

[8] S. Harada, K. Amidaiji and T. Yasunaga, This Bulletin, **45**, 1752 (1972).

[9] J. L. Bear and C. T. Lin, *J. Phys. Chem.*, **72**, 2026 (1968).

[10] H. Hoffmann, *Ber. Bunsenges. Physik. Chem.*, **73**, 432 (1969).

[11] U. Nickel, H. Hoffmann, and W. Jaenicke, *ibid.*, **72**, 526 (1968).

[12] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

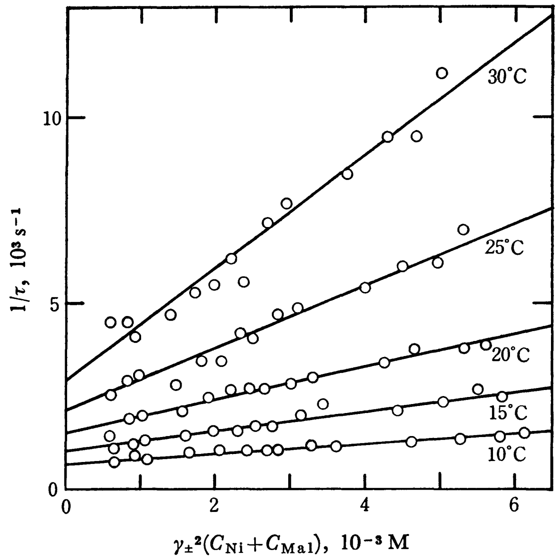


Fig. 1. $1/\tau$ *vs.* $\gamma_\pm^2(C_{\mathrm{Ni}}+C_{\mathrm{Mal}})$ plot at 10, 15, 20, 25, and 30°C.

TABLE 2. THE FORMATION AND DISSOCIATION RATE CONSTANTS AND THE STABILITY CONSTANTS OF NICKEL MALEATE ($\mu \rightarrow 0$)

t, °C	k_f, $\mathrm{M^{-1}\,s^{-1}}$	k_d, $\mathrm{s^{-1}}$	K, $\mathrm{M^{-1}}$
10	1.4×10^5	0.7×10^3	2×10^2
15	2.6×10^5	1.1×10^3	2.5×10^2
20	4.5×10^5	1.5×10^3	3×10^2
25	8.4×10^5	2.1×10^3	4×10^2
30	14.6×10^5	2.9×10^3	5×10^2

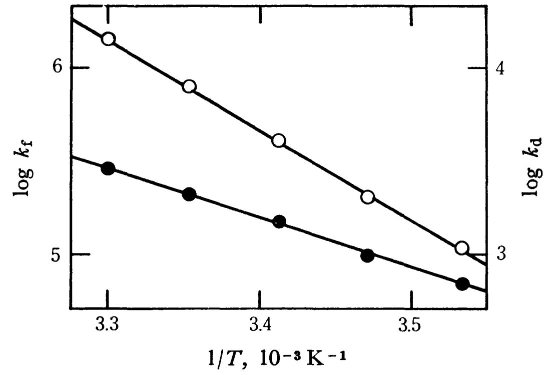


Fig. 2. Temperature dependency of k_f (○) and k_d (●).

TABLE 3. KINETIC DATA OF THE NICKEL MALEATE COMPLEX FORMATION AT 25°C ($\mu \rightarrow 0$)

K, $\mathrm{M^{-1}}$	4×10^2
k_f, $\mathrm{M^{-1}\,s^{-1}}$	8.4×10^5
k_d, $\mathrm{s^{-1}}$	2.1×10^3
$E_f^{\ddagger}$, kcal mol^{-1}	20
$E_d^{\ddagger}$, kcal mol^{-1}	12
$\Delta G_f^{\ddagger}$, kcal mol^{-1}	9
$\Delta H_f^{\ddagger}$, kcal mol^{-1}	19
$\Delta S_f^{\ddagger}$, cal K^{-1} mol^{-1}	34
K_0, $\mathrm{M^{-1}}$	25
k_1, $\mathrm{s^{-1}}$	3.4×10^4

equations; they are listed in Table 3:

$$\log A = \log\frac{eRT}{Nh} + \frac{\Delta S_f^{\ddagger}}{2.3R} \tag{3}$$

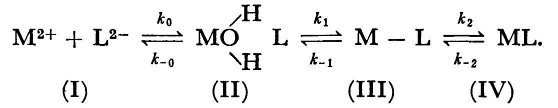
$$\Delta H_f^{\ddagger} = \Delta E_f^{\ddagger} - RT \tag{4}$$

$$\Delta G_{f\ddagger} = \Delta H_f^{\ddagger} - T\Delta S_f^{\ddagger} \tag{5}$$

where A is the frequency factor.

Discussion

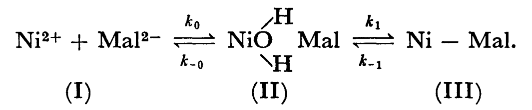
The complex formation reactions between a metal ion and a bidentate ligand have been usually represented by the following mechanism:



$$\underset{\text{(I)}}{\mathrm{M^{2+} + L^{2-}}} \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \underset{\text{(II)}}{\mathrm{M}\overset{\diagup\mathrm{H}}{\underset{\diagdown\mathrm{H}}{\mathrm{O}}}\ \mathrm{L}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(III)}}{\mathrm{M-L}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(IV)}}{\mathrm{ML}}. \tag{6}$$

where (I) is the free ion, (II) is the outer-sphere complex, (III) is the monodentated complex, and (IV) is the bidentated chelate complex.

In the case of the nickel maleate, however, Eq. (6) cannot be applied directly. The stability constants of the nickel dicarboxylate in Table 4 show that the oxalate is a very stable five-membered chelate complex and that the malonate is a less stable six-membered chelate complex. The maleate and the succinate are much less stable, and their stability constants are nearly equivalent to that of the adipate. Moreover, the rate constants of the complex formation and the dissociation of the maleate and the succinate are quite similar to those of the adipate, as is shown in Table 4. Taking into account the fact that the adipate ion does not form a chelate complex,[13] these facts suggest that the maleate and the succinate ions do not form a chelate complex, either. Assuming that the concentration of the chelate complex is negligibly small in comparison with those of the other species, Eq. (6) can be simplified as follows:



$$\underset{\text{(I)}}{\mathrm{Ni^{2+} + Mal^{2-}}} \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \underset{\text{(II)}}{\mathrm{Ni}\overset{\diagup\mathrm{H}}{\underset{\diagdown\mathrm{H}}{\mathrm{O}}}\ \mathrm{Mal}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(III)}}{\mathrm{Ni-Mal}}. \tag{7}$$

In this reaction, the formation of the outer-sphere complex seems to be very fast, so the relaxation time of the rate-determining step of Eq. (7) is given by the equation:

$$1/\tau = \frac{k_1K_0\gamma_\pm^2(C_M+C_L)}{1+K_0\gamma_\pm^2(C_M+C_L)} + k_{-1} \tag{8}$$

where K_0 $(=k_0/k_{-0})$ is the outer-sphere complex formation constant. In the present experiments, $K_0\gamma_\pm^2(C_M+C_L)$ is much smaller than unity; therefore Eq. (8) can be simplified to:

$$1/\tau = k_1K_0\gamma_\pm^2(C_M+C_L) + k_{-1}. \tag{9}$$

Since the concentration of the outer-sphere complex is small, the overall stability constant is given as follows:

$$K = K_0\frac{k_1}{k_{-1}} = \frac{k_f}{k_d}. \tag{10}$$

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[13] H. Hoffmann and E. Yeager, *Ber. Bunsenges. Physik. Chem.*, **74**, 641 (1970).

Table 4. Rates and stability constants of the nickel dicarboxylate complexes at 25°C

Ligand	k_f ($M^{-1} s^{-1}$)	k_d (s^{-1})	K (M^{-1})	μ	Reference
Oxalate	7.4×10^4	3.6	2.1×10^4	0.1	5
	5.2×10^5	3.6	1.4×10^5	—	10
	—	—	2.0×10^5	0.1	4
Malonate	7.0×10^4	44	1.6×10^3	0.1	6
	4.2×10^5	35	1.2×10^4	$\rightarrow0$	9[a]
	—	—	1.6×10^3	0.1	17
Succinate	5.8×10^5	4×10^3	2.1×10^2	$\rightarrow0$	9[a]
	—	—	40	0.1	17
Adipate	8.5×10^3	4×10^3	2.1×10^2	—	10
	—	—	40	0.1	17
Maleate	8.4×10^5	2.1×10^3	4×10^2	$\rightarrow0$	This work
	—	—	1.0×10^2	0.1	17
Malate	5.6×10^5	17	3×10^4	$\rightarrow0$	8

a) The reported rate constant at 20°C was converted to the value at 25°C.

By comparing Eq. (9) with Eq. (2), the following equations were obtained:

$$k_f = k_1 K_0 \tag{11}$$

$$k_d = k_{-1}. \tag{12}$$

The outer-sphere complex formation constant was calculated to be $K_0=25\ M^{-1}$ by the Fuoss equation.[14] Then, k_1 was calculated from k_f and Eq. (11) to be $3.4\times10^4\ s^{-1}$ at 25°C. The value is very close to the water-exchange rate constant on the nickel ion,[15] $k^*=2.7\times10^4\ s^{-1}$. This fact suggests that the rate-determining step of the nickel maleate complex formation is the loss of the water molecule from the inner coordination sphere of the nickel ion. Moreover, the value of k_d is in good agreement with the dissociation rate constant of the nickel maleate, $k_{-1}=2\times10^3\ s^{-1}$, reported by Hoffmann *et al.*[10,16] These coincidences of the data lead to the conclusion that the above procedures are valid.

The kinetic data of the nickel maleate complex formation in Table 3 can be compared with those of other complexes.[5,6,9] $\Delta E_f^{\neq}$, $\Delta H_f^{\neq}$, and $\Delta S_f^{\neq}$ are relatively larger than those of other, analogous nickel dicarboxylate complexes. These differences may be attributed to differences in the stabilities of the outer-sphere complexes. The stability constant can be referred to the literature value at $\mu=0.1$.[17] By dividing the value by $\gamma_{\pm}^2=0.154$, the stability constant at zero ionic strength was estimated to be $650\ M^{-1}$, which was almost the same, within the limits of experimental error, as our result.

The relaxation effects in the nickel dicarboxylate solution have been discussed by two different theories. In one theory,[5,6,8] the monodentated complex formation step, (II)$\rightleftharpoons$(III) in Eq. (6), is considered to be the rate-determining step. On the assumption that C_{II}, $C_{III} \ll C_I, C_{IV}$ and that $k_{-1} \ll k_2$, the rate constants in Eq. (2) were related to the parameters in Eq. (6) as follows:

$$k_f = K_0 k_1 \left(\frac{k_2}{k_2+k_{-1}}\right) \tag{13}$$

$$\simeq K_0 k_1. \tag{14}$$

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right) \tag{15}$$

$$\simeq k_{-1}/K_2. \tag{16}$$

where $K_2=k_2/k_{-2}$. The values of k_1 obtained for many kinds of complexes by means of Eq. (14) are of the order of $\sim10^4\ s^{-1}$, which is very close to the water-exchange rate on the nickel ion;[15] hence, the loss of the water molecule from the inner-coordination sphere of the nickel ion may be considered to be the rate-determining step. The fact that the value of k_d reflects the stabilities of the chelate complexes can be interpreted in terms of Eq. (16), where K_2 shows the stabilities of the chelate. This theory may also be applied to the nickel dicarboxylate complex whose k_f is relatively large ($\gg10^5\ M^{-1}\ s^{-1}$), while at the same time, its k_d is very small. By this theory, Bear *et al.*[9] have assumed that the nickel succinate is a stable chelate complex, *i. e.*, $K_2\gg1$, and have obtained a large value for k_d. It can be seen from Eq. (16), however, that if $K_2\gg1$, k_{-1} will also become very large. The fact is in disagreement with the postulated condition, $k_{-1}\ll k_2$. If $K_2\simeq1$ is assumed, the rate equations become more complicated[18] than Eqs. (1) and (2). In the nickel succinate solution, the relaxation effect has been expressed by a single relaxation and the concentration dependency of τ can be expressed by Eq. (2). This means that the same interpretations should be applied to the succinate as to the maleate system. Moreover, the agreement of k_d with the dissociation rate constant of the succinate,[10,16] $k_{-1}\simeq3\times10^3\ s^{-1}$, indicates that Eq. (12) should be used rather

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[14] R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

[15] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[16] H. Hoffmann and U. Nickel, *Ber. Bunsenges. Physik. Chem.*, **72**, 1096 (1968).

[17] M. Yasuda, K. Yamasaki, and H. Ohtaki, This Bulletin, **33**, 1067 (1960).

[18] G. H. Czerlinski, "Chemical Relaxation," Marcel Dekker Inc., New York, (1966).

than Eq. (16).

On the other hand, Hoffmann *et al.*[10,11] have considered that the rate-determining step of the complex formation is the chelate-ring closure, *i. e.*, (III)$\rightleftharpoons$(IV) in Eq. (6). They assumed that K_0k_1 is constant (8.5×10^5 M^{-1} s^{-1}) for all the nickel dicarboxylates and that the small difference in k_f can be attributed to the $k_2/(k_2+k_{-1})$ term. As can be seen from Eq. (15), however, when k_d becomes relatively large, the k_{-2}/k_2 term increases and C_{III} cannot be neglected in comparison with C_{IV}. This fact disagrees with the assumptions used in deriving Eqs. (13) and (15). Therefore, this procedure can be appropriately applied to a system where $k_f\ll 8.5\times10^5$ M^{-1} s^{-1} and where at the same time, k_d is small.

In summary, when k_d becomes large, $k_d\gtrsim10^3$ s^{-1}, C_{III} cannot be neglected and Eqs. (13) and (15) need to be re-evaluated. In some cases where C_{III} is much larger than C_{IV}, Eqs. (7) to (12) should be applied.