The Kinetics of Complexation of Manganese(II), Cobalt(II), and Nickel(II) Ions with Some Dicarboxylates in Aqueous Solution

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The pressure-jump relaxation method has been used to determine the rate constants for the formation and dissociation of maganese(II), cobalt(II), and nickel(II) with some dicarboxylates in aqueous solution at zero ionic strength. The carboxylate ligands used are 3-nitrophthalate, 4-nitrophthalate, and phenylmalonate. The activation parameters have alse been obtained from the temperature dependence of the rate constants. A dissociative interchange mechanism with a chelate ring closure step as rate determining is employed to interpret the kinetic data of manganese(II) and cobalt(II) complexes. The rates of formation of nickel(II) complexes are controlled by both the solvent exchange step and the chelate ring closure step.

Introduction

The complex formation reactions of the metal ions with the carboxylate ligands are usually very fast so that the kinetic parameters of the complexation can be determined only by the relaxation methods[1]. The high rate of the complexation reaction has been known to be the consequence of the very fast water exchange step taking place between the metal ions and the bulky solvent molecules[1,2].

The study on the mechanism of formation of the labile metal complexes has attracted a great deal of attention[3-20]. The majority of mechanisms of the reactions are well understood by the Eigen mechanism in which the loss of water molecule from the inner coordination sphere of the metal ion is usually considered as the rate determining step. However, the mechanism would be little more complicated by a ring closure process for the chelate ligand systems[5,6].

The complexations of the metal ions with various carboxylate ligands in aqueous solution have been interested since the complexes are used to be a model system for the environmental and biological phenomena[21,22]. Recently, we have carried out a systematic study of the kinetics of formation of various dicarboylate complexes for the bivalent transition metal ions[15-17], which would be the model for the metal complexation of humic substances. We intend to investigate the effect of ligand topology such as the basicity, stereochemical rigidity, and the substituents of the ligands on the kinetic properties of the complexation. In this paper, we report the results of the kinetic investigation on the complexation reactions of manganese(II), cobalt(II), and nickel(II), with 3-nitrophthalate, 4-nitrophthalate, and phenylmalonate.

Experimental

All of chemicals used were of a reagent grade and were used without further purification. Stock solutions of the complexes were prepared and standardized in the same way as that described in the previous paper[15-17]. Each working solution was prepared by diluting the stock solution to desired concentrations. The pH's of the solutions were adjusted to above 5.5 in which most of the ligand acids are existed in the dibasic form.

The kinetic measurements for the complexation reactions were made by means of a pressure-jump technique which was described in some detail previously[18,20]. All relaxation times measured in this study were corrected for the time constant of escaping gas[23]. The measurements were made at 20, 25 and 30℃. An iteration method assuming an initial value of the stability constants of the complex was employed to calculate simultaneously the rate constant and the thermodynamic stability constant of the system from the relaxation times measured at different concentrations.

Results and Discussion

The relaxation processes observed are interpreted in terms of the following complexation reaction of the type,

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

where M^{2+} is the bivalent metal ion, L^{2-}, is the dicarboxylate anion, and ML is the complex. The relaxation time (τ) of the process is related to the forward and reverse rate constants (k_f and k_r) by Eq. (2),

$$\frac{1}{\tau} = k_f f_{\pm}^{2}(\bar{C}_{M^{2+}} + \bar{C}_{L^{2-}}) + k_r \tag{2}$$

where $\bar{C}$ is the equilibrium concentrations of the species and $f_{\pm}$ is the mean activity coefficient of the free ions at a given ionic strength. The activity coefficients of the ions were estimated from the Davies equation[24] which is given by Eq. (3);

$$\log f_i = -0.5 Z_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\ \mu \right) \tag{3}$$

where Z_i is the charge of the ith ion and μ is the ionic strength of the solution.

Eq. (2) shows the plot of $1/\tau$ against $f_{\pm}^{2}(\bar{C}_M 2^{+} + \bar{C}_L 2^{-})$

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Table 1. Relaxation Data for Complexation Reactions of 3-nitrophthalate System at 25℃

Metal ions	Co*×10³ (M)	$\bar{C}_{ML}$×10³ (M)	($\bar{C}_{M^{2+}}=\bar{C}_{L^{2-}}$) ×10³(M)	μ×10⁴	$f\pm$	1τ×10⁻³ (s⁻¹)
Mn	0.92	0.28	0.64	2.57	0.80	5.65
	3.69	1.98	1.71	6.84	0.70	7.75
	5.54	3.33	2.21	8.86	0.67	8.55
	9.23	6.21	3.03	12.10	0.63	9.62
Co	1.01	0.32	0.68	2.14	0.79	3.95
	4.03	2.24	1.80	7.19	0.70	5.46
	6.06	3.74	2.32	9.30	0.67	6.02
	10.08	6.92	3.16	12.64	0.63	6.76
Ni	1.07	0.40	0.67	2.67	0.80	2.99
	2.13	1.05	1.08	4.33	0.75	3.53
	4.26	2.57	1.69	6.77	0.70	4.24
	6.50	4.30	2.19	8.77	0.67	4.69

*Co refers to the total stoichiometric concentrations of the complexes.

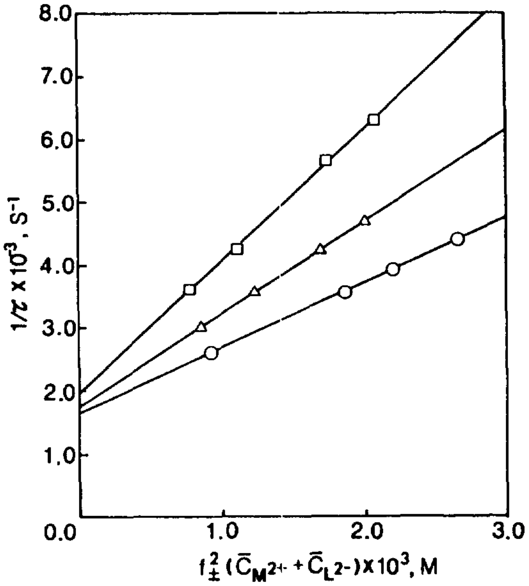

Figure 1. Plot of 1/τ against $f_{\pm}^{2}(\bar{C}_{M^{2+}}+\bar{C}_{L^{2-}})$ for Ni(II)-3-nitrophthalate system at 20 (○), 25 (△), and 30℃ (□).

Table 2. Rate Constants and Stability Constants for Complexation Reactions of 3-nitrophthalate System at μ→0

Temperature (℃)	Metal ions	k_f×10⁻⁵ (M⁻¹s⁻¹)	k_r×10⁻³ (s⁻¹)	K_{eq}×10⁻² (M⁻¹)
20	Mn	16.66±0.19	3.37±0.04	4.95
	Co	12.03±0.06	2.23±0.01	5.40
	Ni	10.37±0.06	1.67±0.01	6.20
25	Mn	24.58±0.41	3.63±0.07	6.78
	Co	17.15±0.12	2.48±0.02	6.92
	Ni	15.14±0.30	1.69±0.04	8.96
30	Mn	36.19±0.19	3.89±0.02	9.31
	Co	25.00±0.42	2.67±0.07	9.35
	Ni	21.08±0.10	1.99±0.01	10.62

gives a linear line of which the slope and the intercept are k_f and k_r respectively. However, we should know the thermodynamic stability constant ($K_{eq}=k_f/k_r$) of the complex in order to calculate the mean activity coefficients and equilibrium concentrations of the ions. Since the accurate values of the thermodynamic stability constants of the complexes studied are needed, we have rather used the iteration method[19] by which the thermodynamic constant and the forward and reverse rate constants are calculated simultaneously from the observed relaxation times and the overall concentrations of the metal and ligand ions.

The typical sets of the final values of the equilibrium concentrations and the mean activity coefficients along with the reciprocals of relaxation times for the 3-nitrophthalate system are given in Table 1. Figure 1 shows the plots of 1/τ against $f_{\pm}^{2}(\bar{C}_{M^{2+}}+\bar{C}_{L^{2-}})$ at various temperature for the Ni(II)-3-nitrophthalate system. The rates and thermodynamic stability constants for various dicarboxylate complexes of some bivalent transition metal ions determined through above procedure are summarized in Table 2. The activation parameters obtained from the Arrhenius plot and Eyring's equation are given in Table 3.

The complex formation reaction is generally understood in terms of the Eigen mechanism[3]. This multistep complexation mechanism has been modified for bidentate ligand systems, considering the chelation step of the complexation[5,6]. The mechanism could be described for the metal complexation reaction with a bidentate ligand in following manner:

$$M^{2+}{}_{(aq)}+L^{2-}{}_{(aq)} \underset{\underset{(I)}{k_{21}}}{\overset{k_{12}}{\rightleftarrows}} W_2MW_1L \underset{\underset{(II)}{k_{32}}}{\overset{k_{23}}{\rightleftarrows}} W_2M\text{-}L \underset{\underset{(III)}{k_{43}}}{\overset{k_{34}}{\rightleftarrows}} M{=}L \quad (4)$$

where W_1 and W_2 are water molecules coordinated in the inner solvation sphere of the metal ion. The step(I) is the diffusion controlled ion pair complex formation. The step(II) involves the loss of a water molecule from the inner solvation sphere of the metal ion and the formation of the monosubstituted metal complex. The step(III) is the formation of the fully chelated complex. The equilibrium constants for the step(I), (II), and (III) are represented by $K_0=k_{12}/k_{21}$, $K_2=k_{23}/k_{32}$, and $K_3=k_{34}/k_{43}$, respectively.

With the assumptions that the step(I) is very rapid compared with other steps and the intermediate $W_2M\text{-}L$ is in a steady state, the overall forward and reverse rate constants (k_f and k_r) of the reaction (1) are related to the rate consants of individual steps of Eq. (4) as:

$$k_f=K_0k_{23}\left(\frac{k_{34}}{k_{32}+k_{34}}\right) \text{ and } k_r=k_{32}\left(\frac{k_{43}}{k_{32}+k_{34}}\right) \quad (5)$$

The complexation reactions of bidentate ligands may be catagorized into two limiting cases[5] which are depending on the ratio of k_{34}/k_{32}. "Limiting case A" is the reaction that the rate determining step is the loss of a water molecule from the inner hydration sphere and ring closure step is much faster, *i.e.*, $k_{34}/k_{32} \gg 1$. In this case, Eq. (5).are reduced to $k_f=K_0k_{23}$ and $k_r=k_{32}/K_3$. The value of k_{23} can be estimated if K_0 is known. The diffusion controlled ion pair formation constant K_0 would be estimated on the theoretical base by the Fuoss equation[25]. Assuming the distance of the closest

Table 3. Activation Parameters for Transition Metal(II) Complex Formation Reactions with Various Dicarboxylates at 25℃ and $\mu \to 0$

Ligands	Metal ions	E_f (kJ·mol^{-1})	$\Delta H_f^{\neq}$ (kJ·mol^{-1})	$\Delta S_f^{\neq}$ (J·mol^{-1}·K^{-1})	$\Delta G_f^{\neq}$ (kJ·mol^{-1})
3-nitro phthalate	Mn	57.3± 2.9	54.8± 2.9	61.5± 2.1	36.4± 3.0
	Co	54.0± 9.2	51.5± 9.2	47.7± 5.0	37.2± 9.3
	Ni	52.3± 9.6	49.8± 9.6	41.0± 4.6	37.7± 9.7
4-nitro phthalate	Mn	49.8± 12.1	47.7± 12.1	32.6± 4.6	37.7± 12.1
	Co	48.1± 33.9	45.6± 33.9	22.6± 9.2	38.9± 34.0
	Ni	46.9± 1.7	44.8± 1.7	18.8± 0.4	38.9± 1.7
Phenyl malonate	Mn	54.4± 38.5	51.9± 38.5	51.5± 21.8	36.4± 39.0
	Co	53.6± 42.7	51.5± 42.7	46.9± 22.2	37.2± 43.2
	Ni	48.1± 25.1	45.6± 25.1	16.3± 5.0	40.6± 25.1

Table 4. Rate Constants of Water Exchange Step (k_{23}) for Transition Metal(II) Complex Formation Reactions with Various Dicarboxylates at 25℃ and $\mu \to 0$

Metal ions	3-nitro-phthalate (s^{-1})	4-nitro-phthalate (s^{-1})	Phenyl-malonate (s^{-1})	Water exchange rate(k_w)[27-30] (s^{-1})
Mn	2.6×10^4	1.6×10^4	2.6×10^4	3.6×10^7
Co	1.8×10^4	1.1×10^4	1.8×10^4	2.6×10^6
Ni	1.6×10^4	9.9×10^3	4.7×10^3	2.7×10^4

approach between two counter ions to be 5 Å[26,27] the value of K_0 at zero ionic strength has been estimated to be 95 M^{-1} at 25℃ for an ion pair of 2+ and 2− ions. Using this value of K_0, the value of k_{23} for the various reaction systems were estimated. They are given in Table 4 along with the literature values[28-31] of the water exchange rate constant (k_w) of the metal ions. The values of k_{23} suppose to be very close to the values of k_w if the systems studied belong to "limiting case A". One can see from Table 4 that each value of k_{23} is at least two order smaller than that of k_w beside the nickel(II) system. This would mean that the condition $k_{34}/k_{32} \gg 1$ does not stand for these systems. However, the values of k_{23} in the nickel(II) system are varied from a ligand to other. This fact suggests that the complexation reactions of manganese(II) and cobalt(II) ions are not the cases for "limiting case A" and the reactions of nickel(II) ion are the intermediate case between "limiting case A" and "limiting case B".

"Limiting case B" is the reaction of which the rate is controlled by the process of the chelate ring formation. In this case, $k_{34}/k_{32} \ll 1$ and thus $k_f = K_0 K_2 k_{34}$ and $k_r = k_{43}$ from Eq. (5). In order to evaluatee the values of k_{34} and k_{43} which are the rate constants for the chelate ring formation process, the values of k_{23} and k_{32} must be known in Eq. (5). The water exchange rate constant for the corresponding metal ions[28-31] k_w could be assumed as k_{23}. The values of k_{32} were estimated using the following semi-empirical relationship between pK_a of the ligand and k_{32} for the metal complexes of dicarboxylate ligands derived by Hoffmann[32] and Yasunaga[12];

$$\log k_{32} = -0.22\ pK_{a2} + A \qquad (6)$$

where A is a constant. Following the Yasunaga's procedure[12], the constant A were obtained to be 4.88, 7.28, and 8.05 for nickel(II), cobalt(II), and manganese(II) systems, respectively. The values of k_{32}, k_{34}, and k_{43} calculated from Eqs. (5) and (6) are listed with equilibrium data in Table 5.

Table 5 shows that the condition $k_{34}/k_{32} \ll 1$ stands for the complexation reactions of manganese(II) and cobalt(II) ions studied. This would mean that the complexation reactions of manganese(II) and cobalt(II) ions belong to "Limiting case B". The rates of chelate ring formation (k_{34}) are at least two order slower than those of the loss of the solvated water molecule from the metal ions (k_w). Again, in the case of Ni(II) complexation systems, the values of k_{34} is very close to the values of k_{32}. This is also an evidence that the reactions of nickel(II) ion would be the intermediate case between "limiting case A" and "limiting case B", which is a concerted

Table 5. Rate and Equilibrium Constants of Each Individual Step of the Multiple Step Complex Formation of Transition Metal(II) with Various Dicarboxylates at 25℃ $\mu \to 0$

Metal ions	Ligands	pK_{a2}	K_{eq}(M^{-1})	k_f(M^{-1}s^{-1})	k_r(s^{-1})	k_w(s^{-1})	k_{32}(s^{-1})	k_{34}(s^{-1})	k_{43}(s^{-1})
Mn	3-nitrophthalate	4.38	6.8×10^2	2.5×10^6	3.6×10^3	3.6×10^7	1.2×10^7	8.8×10^3	3.6×10^3
	4-nitrophthalate	4.44	4.4×10^2	1.5×10^6	3.5×10^3	3.6×10^7	1.2×10^7	5.3×10^3	3.5×10^3
	Phenylmalonate	5.55	1.1×10^3	2.5×10^6	2.4×10^3	3.6×10^7	6.7×10^6	4.9×10^3	2.4×10^3
Co	3-nitrophthalate	4.38	6.9×10^2	1.7×10^6	2.5×10^3	2.6×10^6	1.2×10^6	8.4×10^3	2.5×10^3
	4-nitrophthalate	4.44	4.8×10^2	1.0×10^6	2.2×10^3	2.6×10^6	1.2×10^6	5.1×10^3	2.2×10^3
	Phenylmalonate	5.55	1.1×10^3	1.7×10^6	1.5×10^3	2.6×10^6	6.7×10^5	4.6×10^3	1.5×10^3
Ni	3-nitrophthalate	4.38	8.9×10^2	1.5×10^6	1.7×10^3	2.7×10^4	8.3×10^3	1.2×10^4	4.1×10^3
	4-nitrophthalate	4.44	5.6×10^2	9.4×10^5	1.7×10^3	2.7×10^4	8.1×10^3	4.7×10^3	2.6×10^3
	Phenylmalonate	5.55	1.3×10^3	4.5×10^5	3.6×10^2	2.7×10^4	4.6×10^3	9.7×10^2	4.3×10^2

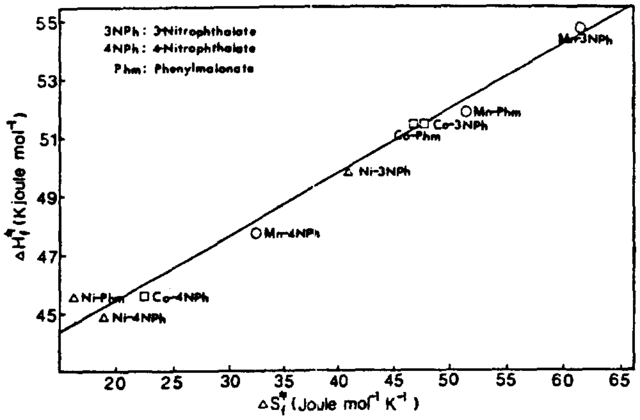

Figure 2. Isokinetic plot for 1 : 1 complex formation reactions of some metal(II)-dicarboxylates.

mechanism between k_{23} and k_{34}. However, that k_{34} values for nickel(II) systems are a little smaller than k_w values of nickel(II) ion implies that the mechanism of the reaction inclines to some extent to "limiting case B" depending on the nature of the ligands.

Although the rates of ring formation and rupture are varied from a ligand to other, it does not reveal that there is a significant effect by the nitro substituent of the phthalate ligands. The large positive entropy of activation of the reactions in Table 3 indicates an Id mechanism for the reactions as usual. Figure 2 is the isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ of the complexation reactions studied. A good linearity of the isokinetic relationship is observed. The isokinetic temperature resulted from the slope of the linear line was calculated to be 217°K which is lower than the reaction temperature. This supports that the complexation reactions of the dicarboxylate ligands studied would be controlled by the activation entropy and thus an Id mechanism is designated.

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References

1. D. W. Margerum, G. R. Cayley, D. C. Weatherburm, and G. K. Pagenkopf, in A. E. Martell (ed.), *Coordination Chemistry*, Vol. 2, American Chemical Society, Washington, DC, 1978, Ch. 1.
2. C. Cossy, L. Helm, and A. E. Merbach, *Inorg. Chem.*, **27**, 1973 (1988).
3. M. Eigen and R. G. Wilkins, ***Advances in Chemical Series***, No. 49, American Chemical Society, Washington, DC., 1965.
4. K. Kustin and J. Swinhart, *Prog. Inorg. Chem.*, **13**, 107 (1970).
5. K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.*, **88**, 4610 (1966).
6. A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Am. Chem. Soc.* **89**, 3126 (1967).
7. T. M. Che and K. Kustin, *Inorg. Chem.*, **20**, 509 (1981).
8. L. A. Dominey and K. Kustin, *Inorg. Chem.*, **23**, 103 (1984).
9. J. L. Bear and C. T. Lin, *J. Phys. Chem.*, **72**, 2026 (1968).
10. S. Harada, H. Tanabe, and T. Yasunaga, *Bull. Chem. Soc. Jap.*, **46**, 2450 (1973).
11. K. Tamura, S. Harada, and T. Yasunaga, *Bull. Chem. Soc. Jap.*, **50**, 2317 (1977).
12. S. Harada, M. Kawasawa, and T. Yasunaga, *Bull. Chem. Soc. Jap.*, **53**, 2074 (1980).
13. T. Inoue, K. Sugahara, K. Kojima, and R. Shimazawa, *Inorg. Chem.*, **22**, 3972 (1983).
14. T. Inoue, K. Sugahara, K. Kojima, and R. Shimazawa, *Inorg. Chem.*, **22**, 3977 (1983).
15. S. S. Yun, K. Y. Choi, and C. H. Park, *Polyhedron*, **7**, 203 (1988).
16. S. S. Yun and K. Y. Choi, *Int. J. Chem. Kinetic*, **21**, 1131 (1989).
17. K. Y. Choi, S. S. Yun, and M. J. Kim, *Bull. Kor. Chem. Soc.*, **12**, 629 (1991).
18. S. S. Yun, S. H. Kim, J. M. Yang, and K. Y. Choi, *Bull. Kor. Chem. Soc.*, **10**, 155 (1989).
19. G. Macri and S. Petrucci, *Inorg. Chem.*, **9**, 1009 (1970).
20. G. R. Painter and B. C. Pressman, in F. L. Boschke (ed..), ***Topics in Current Chemistry***, Vol. 101, Springer-Verlag, 1982, p. 83.
21. R. B. Lauffer, *Chem. Rev.*, **87**, 901 (1987).
22. M. Eigen and L. DeMaeyer, ***Investigations of Rates and Mechanisms of Reactions***, in S. Friess, E. Lewis, and A. Weissberger (ed.), *Technique of Organic Chemistry*, Vol. 8, Part 2, Interscience, New York, 1963.
23. C. W. Davies, *Ion Association*, Butterworth, London, 1962.
24. R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
25. G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).
26. K. Kustin and J. L. McClean, *J. Phys. Chem.*, **82**, 2549 (1978).
27. T. Swift and R. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
28. D. B. Bechtold, G. Liu, H. W. Dodgen, and J. P. Hunt, *J. Phys. Chem.*, **82**, 333 (1978).
29. A. H. Zeltmann, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.* **73**, 2689 (1969).
30. P. E. Hoggard, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **5**, 959 (1971).
31. H. Hoffmann, *Ber. Bunsenges, Phys. Chem.*, **73**, 432 (1969).