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Kinetic Studies of Copper(II) Chloroacetate Complex Formation Reaction in Aqueous Solutions

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Rate constant of the complex formation reaction depends on the nature of the metal ion, *e.g.*, on the charge, the electronic configuration, the ionic radius, and the coordination structure.[1] The development of the relaxation methods has made it possible to study kinetically on many complex formation reactions which proceed too fast to be studied by the conventional method. On copper(II) complex formation reaction, however, relatively few kinetic studies have been carried out.[2,3] This is presumably because of the fast rate of the reaction and ease of the formation of hydroxy species even at relatively low pH's. The purpose of the present investigation is to study on the copper(II) chloroacetate complex formation reaction, which can be studied at low pH's, with the help of the ultrasonic absorption method.

Experimental

Reagent-grade copper nitrate, chloroacetic acid, sodium hydroxide, and sodium perchlorate were used. The ionic strength of the solutions was adjusted to 1.0 by an addition of sodium perchlorate. Ultrasonic absorption measurements were carried out at 25°C by the pulse method over the frequency range from 5.5 to 220 MHz. Details of the apparatus have been described elsewhere.[4]

Theoretical

The metal ion and the ligand are hydrated in an aqueous solution. In the case of the complex formation, therefore, two or three-step mechanisms, the rate-determining step of which is the release of a water molecule from the metal ion, have been proposed;[5]

$$\underset{\text{(I)}}{\mathrm{M}_{\mathrm{aq}}^{m+} + \mathrm{L}_{\mathrm{aq}}^{n-}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{(II)}}{\left[\mathrm{M}^{m+}\mathrm{O}\langle{}^{\mathrm{H}}_{\mathrm{H}}\mathrm{L}^{n-}\right]_{\mathrm{aq}}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{(III)}}{[\mathrm{ML}]_{\mathrm{aq}}^{m-n}} \qquad (1)$$

where M is the metal ion, L is the ligand, state I is free ions, state II is the ion-pair, and state III is the complex, and the subscript means that the ions are hydrated. Step I—II represents the diffusion of the ions to form the ion-pair and the rate constants, k_{12}, k_{21}, seem to be very fast. Step II—III is the rate-determining process of the inner-sphere complex formation. With the assumption that k_{12}, $k_{21} \gg k_{23}$, k_{32}, the relaxation frequency, f_r, for the step II—III is related to the rate constants and the ionic concentrations by the following form;

$$2\pi f_r = k_{32} + k_{23}\{1 + k_{21}/k_{12}(C_{\mathrm{M}} + C_{\mathrm{L}})\}^{-1} \qquad (2)$$

where C_{M} and C_{L} are the concentrations of M and L respectively. The relaxation absorption is expressed by the single relaxation equation;

$$\alpha/f^2 = A\{1 + (f/f_r)^2\}^{-1} + B \qquad (3)$$

where α is the absorption coefficient, f is the frequency, and A and B are constants.

Results and Discussion

The concentrations of the species, which were calculated by the use of the formation constants of copper(II) chloroacetate[6] are summarized in Table 1. Representative absorption curves are shown in Fig. 1. The relaxation frequencies obtained are also listed in

TABLE 1. EXPERIMENTAL CONDITIONS AND THE RELAXATION FREQUENCY OF THE SOLUTION

Sample number	$\sum$Cu (10^{-1} M)	$\sum$L (10^{-1} M)	Ionic concentrations (10^{-3} M)					f_r (MHz)
			L	Cu	CuL	$\mathrm{CuL_2}$	$\mathrm{CuL_3}$	
1	1	1	61	65	32	3	—	37
2	1	2	130	43	45	9	3	40
3	1	3	200	30	49	14	7	44
4	2	2	92	107	80	11	2	49
5	2	3	145	79	93	21	7	45
6	3	1	32	236	61	3	—	56
7	3	2	70	183	104	11	2	53
8	3	3	110	144	129	22	5	53
9	3	5	73	300	178	19	3	58
10	3	7	54	475	208	15	2	65

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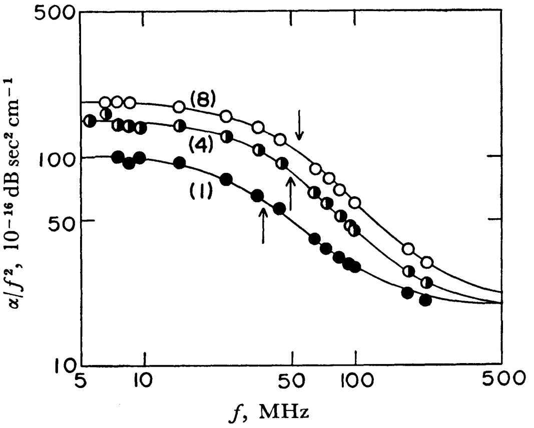

Fig. 1. Ultrasonic absorption in copper(II) chloroacetate solutions. The arrows indicate the relaxation frequencies. Numeral shows the sample number.

Table 1. To ensure that the observed relaxation absorption is due to the complex formation reaction of copper(II) chloroacetate, blank experiments were carried out with solutions containing copper(II) nitrate or chloroacetic acid in the same conditions. In no case was a relaxation absorption observed.

The principal equilibria between copper and chloroacetate ions at low concentrations are;

$$Cu^{2+} + ClAc^- \rightleftharpoons Cu(ClAc)^+ \qquad (4)$$

$$Cu(ClAc)^+ + ClAc^- \rightleftharpoons Cu(ClAc)_2 \qquad (5)$$

where $ClAc^-$ means the chloroacetate ion. $Cu(ClAc)_3{}^-$ and higher-order complexes may exist, but the concentrations are very low. Both of the equations have been investigated in trying to correlate the experimental data. In applying Eq. (2) to Eq. (4), the ratio k_{12}/k_{21}, which is the ion-pair constant K_0, can be estimated using the Fuoss equation.[7,8] At ionic strength 1.0, K_0 is calculated to be about 1 for the 2—1 electrolytes. With the data in Table 1 and K_0, f_r is plotted against $[1+1/\{K_0(C_{Cu^{2+}}+C_{ClAc^-})\}]^{-1}$ in Fig. 2. From the slope and the intercept of the line in Fig. 2, k_{23} and k_{32} were obtained; $k_{23}=8.5\times10^8$ sec^{-1}, and $k_{32}=1.4\times10^8$ sec^{-1}. Over-all formation constant, K, can be approximately given by $K_0(1+k_{23}/k_{32})$ and is calculated to be; 7.1 M^{-1}. Taking into account the uncertainty of K_0, this value is in good agreement with the value reported in Ref. 6, 8.1 M^{-1}, which had been previously used in the calculation of the ionic concentrations. On the other hand, the same plots for Eq. (5) do not show a linear relation. These results suggest that Eq. (4) is responsible for the present absorption.

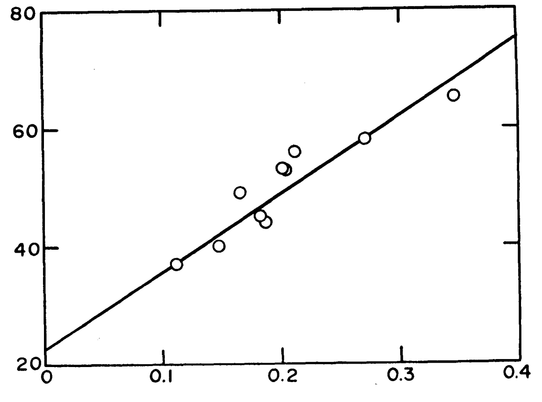

Fig. 2. Plot of relaxation frequency (f_r) *vs.* $[1+1/\{K_0(C_M+C_L)\}]^{-1}$.

By the ultransonic absorption measurements in the aqueous solution of copper(II) acetate, the rate constant of water substitution of Cu^{2+} ion is reported[9]; $k_{H_2O}=(1—2)\times10^9$ sec^{-1}.

The rate constant k_{23} of copper(II) chloroacetate complex formation reaction obtained above is very close to the value in the case where the ligand is acetate. Moreover the rate constant k_{23} is also close to the water substitution rate studied by the NMR; $k_{ex}\gtrsim3\times10^9$ sec^{-1}. These facts show that the rate-determining step of the complex formation reaction is the loss of a water molecule from the inner-sphere of the metal ion.

As is well known, the d^9 copper(II) ion is subject to Jahn-Teller distortion, and the axial water molecules are in a great lability. Consequently, the fast water substitution rate of copper(II) obtained above may be mainly caused by its peculiar electronic configuration.

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