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Kinetic Studies of Lead Acetate Complex Formation in Aqueous Solutions

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It is well known[1] that the rate constant of complex formation depends on the nature of the metal ion, *e.g.*, on the charge, the electric configuration, the ionic radius, and the coordination number. The Pb^{2+} ion has a noble gas electronic configuration and a large ionic radius; therefore, the rate of water substitution, which is the rate-determining step of the complex formation reaction, is expected to be very fast. The purpose of the present work is to perform kinetic studies of lead acetate complex formation with the help of the ultrasonic relaxation method.

Experimental

Reagent-grade lead acetate, lead nitrate, sodium acetate, and perchloric acid were used. Ultrasonic absorption measurements were carried out at 25°C by the pulse method over the frequency range from 15 to 95 MHz. Details of the apparatus have been described elsewhere.[2]

Theoretical

The metal ion and the ligand are hydrated in an aqueous solution. In the case of 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.[3,4] If the substitution rate of the water molecule is fast, however, the distinction of the steps is obscured. The complex formation reaction can, then, be approximately expressed by:

$$M^{m+}_{aq} + L^{n-}_{aq} \overset{k_b}{\underset{k_f}{\rightleftarrows}} ML^{m-n}_{aq} \qquad (1)$$

where M is the metal ion, L is the ligand, and ML is the complex, and where the subscript means that the ions are hydrated. The rate constants are related to the relaxation frequency, f_r, by the following form:

$$2\pi f_r = k_f + k_b(C_M + C_L) \qquad (2)$$

where C_M and C_L are the concentrations of M and L respectively. The relaxation frequency 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 lead acetate[5,6] and acetic acid,[7] are summarized in Table

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[1] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

[2] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

[3] M. Eigen and K. Tamm, *Z. Elektrochem.*, *Ber. Bunsenges. Phys. Chem.*, **66**, 93, 107 (1962).

[4] M. Eigen, *ibid.*, **67**, 753 (1963).

[5] N. Tanaka and K. Kato, This Bulletin, **33**, 417, 1412 (1960).

[6] E. A. Burns and D. N. Hume, *J. Amer. Chem. Soc.*, **78**, 3958 (1956).

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

Table 1. Experimental conditions and the relaxation frequency of the solution

Sample Number	$\sum$ Pb (10^{-3} M)	$\sum$ Ac (10^{-3} M)	pH	Concentration of the species (10^{-3} M)					f_r (MHz)
				Ac^-	Pb^{2+}	$PbAc^+$	$Pb(Ac)_2$	$Pb(Ac)_3^-$	
1	5	10	5.00	6	3	2	—[a]	—	25
2	15	30	4.82	12	6	9	1	—	37
3	15	50	4.72	20	4	10	1	—	35
4	25	50	4.97	20	6	17	2	1	48
5	50	30	4.58	5	30	19	1	—	50
6	50	50	5.00	12	19	29	2	—	47
7	50	100	5.02	35	8	34	7	1	61
8	50	150	5.01	63	4	32	12	2	63
9	75	50	4.55	20	6	17	2	—	53
10	75	150	5.03	47	8	50	14	2	77
11	100	50	4.58	5	61	38	1	—	82
12	100	200	4.91	54	9	66	21	4	85

a) 0.1×10^{-3} M

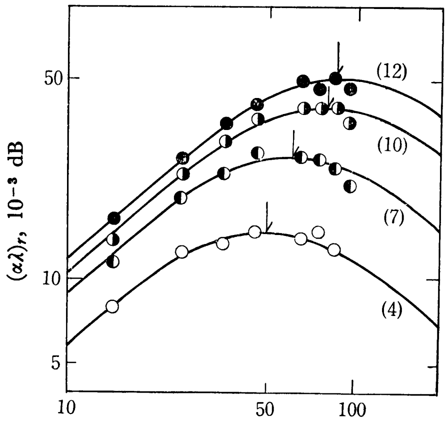

Fig. 1. Ultrasonic absorption in lead acetate solutions. $(\alpha\lambda)_r$ means the excess absorption per wavelength and the arrows indicate the relaxation frequencies. Numeral shows the sample number.

1. The ionic strengths of the solutions were 0.1—0.3, but the formation constant of lead acetate at $\mu=0.2$ was used, for the change in ionic strength by an addition of $NaClO_4$ did not have a serious effect on the absorption curves. Therefore, no special care was taken with regard to the ionic strength. Representative absorption curves are shown in Fig. 1. The relaxation frequencies obtained are also listed in Table 1.

The principal equilibria between lead and acetate ions at low concentrations are:

$$Pb^{2+} + Ac^- \underset{k_{f1}}{\overset{k_{b1}}{\rightleftarrows}} PbAc^+ \tag{4}$$

$$PbAc^+ + Ac^- \underset{k_{f2}}{\overset{k_{b2}}{\rightleftarrows}} Pb(Ac)_2 \tag{5}$$

$Pb(Ac)_3^-$ and higher-order complexes may exist, but the concentrations are very low. Therefore, the present absorption can be attributed to one of the above two equilibria. Both of the equations have been investigated in trying to correlate the experimental data. Equation (2) can, then, be rewritten for Eq. (4):

$$2\pi f_r = k_{f1} + k_{b1}(C_{Pb^{2+}} + C_{Ac^-}) \tag{6}$$

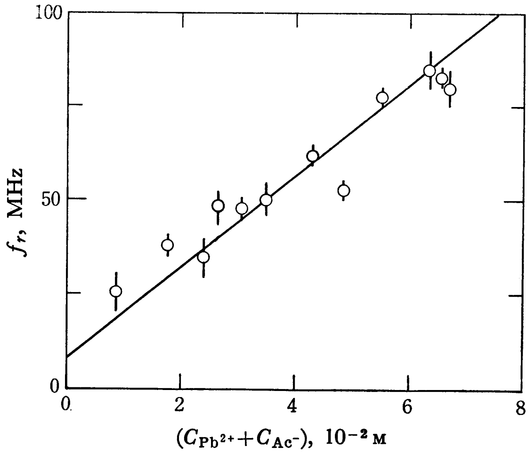

Fig. 2. Plot of relaxation frequency (f_r) vs. $(C_{Pb^{2+}}+C_{Ac^-})$.

With the data in Table 1, f_r is plotted against $(C_{Pb^{2+}}+C_{Ac^-})$ in Fig. 2. From the slope and the intercept of the line in Fig. 2, k_{b1} and k_{f1} were obtained; $k_{b1}=7.5\times10^9$ M^{-1}sec^{-1}, and $k_{f1}=5.7\times10^7$ sec^{-1}. The equilibrium constant of Eq. (4) is also given by $K=k_{b1}/k_{f1}=133$ M^{-1}. The equilibrium constant obtained is in good agreement with the literature value,[5,6] which had been previously used in the calculation of the ionic concentrations. On the other hand, the same plots for Eq. (5) show a linear relation, but yield a different equilibrium constant from that used before. Along with the fact that the excess ultrasonic absorption was observed in the solution where the concentration of $PbAc_2$ was very low, these results suggest that Eq. (4) is responsible for the present absorption.

The formation rate constant of Eq. (4), k_{b1}, is interesting in relation to the nature of the metal ion. Eigen and Eyring[8] obtained the rate constant of complex formation, $k_b=7\times10^9$ M^{-1}sec^{-1}, for the reaction:

$$HgCl^+ + Cl^- \underset{k_f}{\overset{k_b}{\rightleftarrows}} HgCl_2 \tag{7}$$

They said that the value is close to the rate constants of water substitution of Pb^{2+} and Ba^{2+} ions. In this

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[8] M. Eigen and E. M. Eyring, *Inorg. Chem.*, **2**, 636 (1963).

work, we obtained 7.5×10^9 M^{-1} sec^{-1} for the rate constant of the complex formation of lead acetate. Considering that the Pb^{2+} ion has a large ionic radius[9] (1.32 Å) and the filled outer orbitals and, moreover, considering that the coordination number of the water molecule is larger than those of ordinary ions,[10] the above value seems to be reasonable.

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[9] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," J. Wiley & Sons, Inc., New York (1958). p. 66.

[10] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).