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Kinetic Studies of the Aluminium Acetate Complex Formation Reaction in Aqueous Solutions by the Pressure-Jump Method

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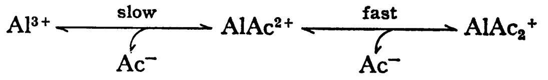
The pressure-jump method was applied to aqueous solutions of aluminium acetate. Relaxation effects were observed in ms and s regions. Both relaxation times depend a great deal on the pH of solution. They were ascribed to the following complex formation reactions.



$$\mathrm{Al^{3+}} \underset{\mathrm{Ac^-}}{\overset{\text{slow}}{\longleftrightarrow}} \mathrm{AlAc^{2+}} \underset{\mathrm{Ac^-}}{\overset{\text{fast}}{\longleftrightarrow}} \mathrm{AlAc_2^{+}}$$

Detailed studies on the fast relaxation effect revealed that the hydrolyzed ionic species accelerate the overall reaction. The mechanism of the fast reaction was discussed, the kinetic parameters being obtained.

The relaxation method mainly developed by Eigen *et al.*[1] has made it possible to study kinetically the fast metal complex formation reaction. Considerable kinetic information now exists on the complexations of metal ions with organic and inorganic ligands.[2,3] Many relaxation phenomena can be interpreted by the step-by-step association picture.

On the complexation of aluminium ion, a few kinetic studies have so far been reported, such as pressure-jump studies of aluminium sulfate[4,5] and aluminium ferricyanide.[6] The present study was undertaken in order to obtain kinetic information on the complex formation reaction of aluminium ion with acetate ion by means of the pressure-jump method at different concentrations, acidities and temperatures.

Experimental

Chemicals of reagent grade were used without purification. A stock solution of aluminium acetate was prepared by mixing a stoichiometric amount of $Al_2(SO_4)_3$ with barium acetate and removing the $BaSO_4$ produced by centrifugation. Barium acetate was prepared by neutralizing acetic acid with $Ba(OH)_2$. The concentration of aluminium in the resulting solution was gravimetrically determined by means of oxine precipitation. Each solution was prepared by diluting the standard solution with an acetic acid solution of known concentration to the desired concentration and pH. No supporting electrolyte was added in order to avoid a decrease in relaxation amplitude.

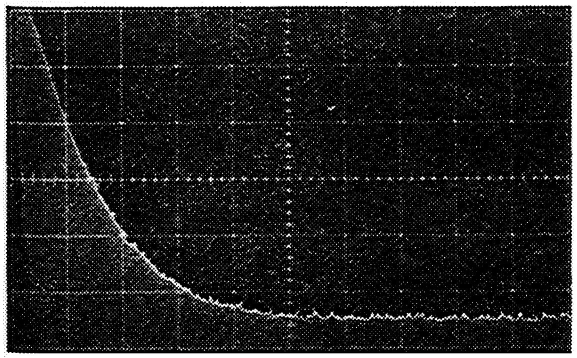


Fig. 1. Pressure-jump relaxation spectrum of the aluminium acetate system at 25 °C: $\sum \mathrm{Al}=2.46\times10^{-3}$ M, $\sum \mathrm{Ac}=0.105$ M, pH=3.76; sweep 20 ms/div.

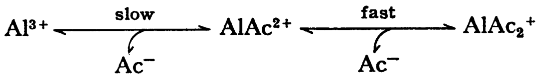
The measurement of the relaxation effect was carried out by pressure-jump technique with a conductivity readout. A representative relaxation spectrum in ms region is shown in Fig. 1. The apparatus realizes a pressure jump of about 100 atm within 100 μs.[7] The temperature of the sample was controlled to ±0.1 °C by circulating thermostated water around the pressure-jump cell.

Results and Discussion

Two relaxation phenomena were observed in all the aluminium acetate solutions: a fast reaction with ms order time constant and a slow reaction with s order time constant. Both relaxation times depend a great deal on the pH of the solution.

In the blank test, neither $Al(NO_3)_3$ nor acetic acid aqueous solution showed relaxation phenomena under the same experimental conditions and in the same time region. This indicates that the relaxation effects observed in the aluminium acetate system can be ascribed to the complex formation reaction of aluminium ion with acetate ion, and are not directly associated with either the hydrolysis reaction of aluminium ion or the dissociation reaction of acetic acid.

In comparison with the rate constants of the water exchange reaction of aluminium ion measured by NMR[8,9] and those of the complex formation reaction of other aluminium complexes,[4–6] the relaxation effects observed in the present experiment are attributed to the following reactions.



$$\mathrm{Al^{3+}} \underset{\mathrm{Ac^-}}{\overset{\text{slow}}{\longleftrightarrow}} \mathrm{AlAc^{2+}} \underset{\mathrm{Ac^-}}{\overset{\text{fast}}{\longleftrightarrow}} \mathrm{AlAc_2^{+}} \qquad (1)$$

Two series of measurements were performed: (i) variation of pH by the addition of acetic acid, the total concentration of aluminium being kept constant (Table 1) and (ii) variation of the total concentrations of aluminium and acetic acid, the pH being kept at 3.76 (Table 2). The reciprocal relaxation times represent an average of at least four runs, the maximum errors being less than ±10%.

In the present study, the following equilibria are assumed to be present.

$$\mathrm{Al^{3+} + Ac^- \overset{K_1}{\rightleftharpoons} AlAc^{2+}} \qquad (2)$$

Table 1. Reciprocal relaxation times and experimental conditions for the aluminium acetate system at constant $\sum$Al of 0.99×10^{-2} M

$\sum$Ac, M	pH	τ^{-1}, s^{-1} 20 °C	τ^{-1}, s^{-1} 25 °C	τ^{-1}, s^{-1} 30 °C
0.0670	4.43	109.5	179.2	349.8
0.0839	4.25	77.18	135.3	277.1
0.1069	4.15	64.06	120.6	213.0
0.1452	4.02	45.77	85.68	162.0
0.1834	3.90	37.46	71.18	146.8
0.2599	3.78	29.89	58.01	115.2
0.3365	3.61	25.84	47.34	103.0
0.4895	3.50	20.80	40.01	73.61
0.6043	3.28	18.72	35.38	74.16
1.2295	3.13	16.04	29.07	57.54
1.4293	3.06	15.86	32.05	55.35

Table 2. Reciprocal relaxation times and experimental conditions for the aluminium acetate system at constant pH of 3.76

$\sum$Al, 10^{-2} M	$\sum$Ac, M	τ^{-1}, s^{-1} 20 °C	τ^{-1}, s^{-1} 25 °C
1.98	0.4605	32.00	60.24
0.981	0.2763	24.93	48.30
0.487	0.1770	22.10	44.89
0.246	0.1054	19.66	39.98
0.124	0.0808	15.10	32.90
0.0625	0.0468		24.11

$$\mathrm{AlAc^{2+} + Ac^- \underset{}{\overset{K_2}{\rightleftharpoons}} AlAc_2^+} \tag{3}$$

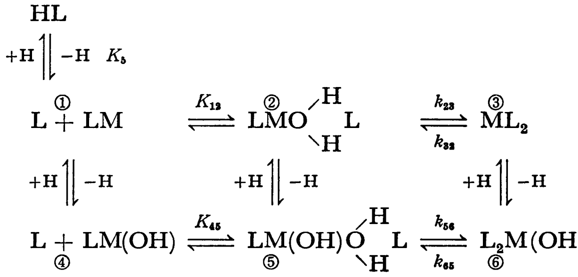
$$\mathrm{Al^{3+} + H_2O \overset{K_3}{\rightleftharpoons} AlOH^{2+} + H^+} \tag{4}$$

$$\mathrm{AlOH^{2+} + Ac^- \overset{K_4}{\rightleftharpoons} Al(OH)Ac^+} \tag{5}$$

$$\mathrm{HAc \overset{K_5}{\rightleftharpoons} Ac^- + H^+} \tag{6}$$

In order to analyze the kinetic data and elucidate the reaction mechanism, it is necessary to evaluate the equilibrium concentrations of each ionic species in solution. For this purpose, the equilibrium constants of Eqs. 2—6 should be known. However, no stability constants of aluminium acetate complexes are found in literature. The equilibrium constants of equilibria 2 and 3 were evaluated to be the same as those of the propionate ligand,[10] *i.e.*, $K_1=60\ \mathrm{M^{-1}}$ and $K_2=43\ \mathrm{M^{-1}}$. The other equilibrium constants were taken from literature as follows. $K_3=10^{-5.0}$ M,[11] $K_4=10^{2.4}\ \mathrm{M^{-1}}$[12] and $K_5=10^{-4.7}$ M.[13] The result of calculations revealed that the concentrations of the hydrolyzed species $\mathrm{AlOH^{2+}}$ and $\mathrm{Al(OH)Ac^+}$ are very small as compared to those of unhydrolyzed complex ions and can be neglected.

If we take account of the fact that the relaxation times in the present system depend a great deal on the concentration of the hydrogen ion, the overall mechanism of Eq. 3 can be expressed by the following reaction scheme.



(7)

where L is the ligand (=acetate ion), LM the metal complex ion (=$\mathrm{AlAc^{2+}}$), K_{12} and K_{45} are the outer-sphere complex formation constants.

All the vertical steps are protolytic reactions and very fast, while in the horizontal steps the outer-sphere complex formation reactions (①⇌② and ④⇌⑤) are fast as compared to the inner-sphere complex formation reactions. Thus, the reactions within the coordination sphere (②⇌③ and ⑤⇌⑥) are the rate-determining steps of the complex formation. The reciprocal relaxation time for this system, then, is given by

$$\tau^{-1} = A(k_{32} + k_{65}K_{36}/C_{\mathrm{H}}), \tag{8}$$

where K_{36} is the hydrolysis constant of inner-sphere complex and

$$A = 1 + K_{23}\cdot\frac{K_{12}\{C_{\mathrm{LM}}/(1+\alpha)+C_{\mathrm{L}}\}}{1+K_{12}\{C_{\mathrm{LM}}/(1+\alpha)+C_{\mathrm{L}}\}}, \tag{9}$$

with
$$\alpha = \frac{C_{\mathrm{H}}}{K_5 + C_{\mathrm{L}}}. \tag{10}$$

From calculation of ionic concentrations, α was found to be smaller than unity under the present experimental conditions. Thus, Eq. 9 becomes

$$A = 1 + K_{23}\cdot\frac{K_{12}(C_{\mathrm{LM}}+C_{\mathrm{L}})}{1+K_{12}(C_{\mathrm{LM}}+C_{\mathrm{L}})}. \tag{11}$$

In order to use this equation, the values of K_{23} and K_{12} should be known. K_{12} was estimated by means of the Fuoss equation.[14,15] K_{23} is related to K_{12} as regards

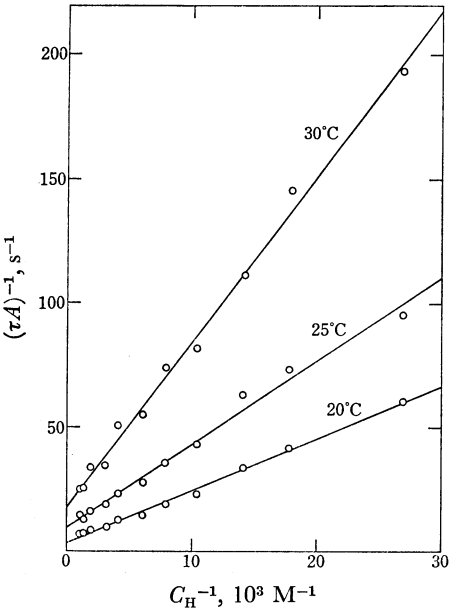


Fig. 2. $(\tau A)^{-1}$ *vs.* C_{H}^{-1} plot at various temperatures. $\sum$Al was kept constant to be 0.99×10^{-2} M.

the conventional stability constant K_2 as follows:

$$K_2 = K_{12}(1 + K_{23}). \tag{12}$$

In the pH variation measurement, the values of $(\tau A)^{-1}$ are plotted against C_H^{-1} to give k_{32} and $k_{65}K_{36}$ from the intercept and the slope of the line, respectively. Plots of values in Table 1 lie on straight lines for each temperature (Fig. 2). Taking into account the small variation of A, *i.e.*, 1.8—2.3, τ^{-1} depends predominantly on the concentration of the hydrogen ion and only slightly on those of other ionic species. Thus, k_{32} and $k_{65}K_{36}$ were obtained from Fig. 2 and k_{23} was calculated by means of the relation $K_{23}=k_{23}/k_{32}$. The values obtained are given in Table 3.

TABLE 3. KINETIC DATA FOR THE ALUMINIUM ACETATE COMPLEX FORMATION REACTION OF MECHANISM (7) AT 25 °C AND μ=0.03

K_{12}	M^{-1}	2.9
K_{23}		13.9
k_{23}	s^{-1}	132
k_{32}	s^{-1}	9.5
$\Delta E^{\ddagger}_{32}$	kcal mol^{-1}	29.9
$\Delta H^{\ddagger}_{32}$	kcal mol^{-1}	29.3
$\Delta S^{\ddagger}_{32}$	cal deg^{-1} mol^{-1}	46.6
$k_{65}K_{36}$	M s^{-1}	0.0034

In the pH constant measurement, the terms in parenthesis of Eq. 8 remain constant, τ^{-1} being affected only by A. Under the present conditions of pH 3.76, the ratio of $k_{65}K_{36}/C_H$ to k_{32} was found to be 2.0 at 25 °C (Fig. 2). Applying this ratio to Eqs. 8 and 11, the following equation is obtained as an empirical formula at pH 3.76 and 25 °C:

$$\tau^{-1} = 3.0 \left\{ k_{32} + k_{23} \cdot \frac{K_{12}(C_{LM} + C_L)}{1 + K_{12}(C_{LM} + C_L)} \right\}. \tag{13}$$

The values of τ^{-1} in Table 2 are plotted against $K_{12}(C_{LM}+C_L)/\{1+K_{12}(C_{LM}+C_L)\}$ and are shown in Fig. 3. The intercept and the slope of the straight line gave k_{32} and k_{23} to be 7.4 and 112 s^{-1} respectively, K_{23} being calculated to be 15.0 by means of the relation $K_{23}=k_{23}/k_{32}$. The values are comparable to those in Table 3. The fact that the values of the rate constants obtained in two different measurements coincide approximately indicates that reaction mechanism 7 and the relaxation formulas are reasonable.

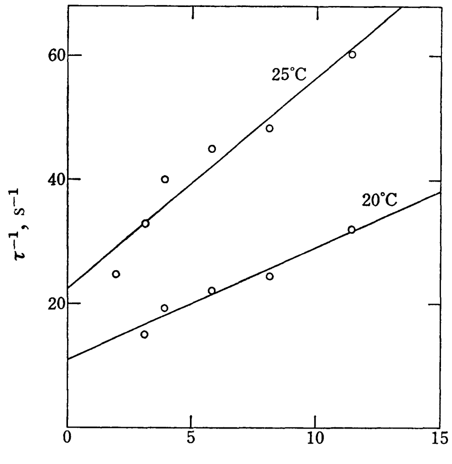


Fig. 3. τ^{-1} *vs.* $K_{12}(C_{LM}+C_L)/\{1+K_{12}(C_{LM}+C_L)\}$ plot at 25 °C. pH was kept constant to be 3.76.

In the aqueous solutions of aluminium ion and its complex ions, the rate constant of the coordinated water exchange, k_{H_2O}, has also been measured by means of NMR. The value of k_{H_2O} of Al^{3+} is about 1 s^{-1},[8] smaller by a factor of 10^2 than that of k_{23}. This is why the slow relaxation effect was attributed to equilibrium 2 and the fast to equilibrium 3. Although k_{23} should be discussed in comparison with k_{H_2O} of $AlAc^{2+}$ ion, the value of the latter has not been found in literature. In the DMF solutions of Al^{3+} and $Al(acac)^{2+}$, the rate constants of the coordinated solvent molecule exchange have been reported. The value of $Al(acac)^{2+}$[16] is accelerated by a factor of 10^2 as compared to that of Al^{3+}.[17] This increment may be caused by the instabilization of the coordinated solvent molecule owing to the electrostatic charge effect. Applying the same idea to the aqueous solution system of aluminium acetate, the value of k_{23} may be recognized as the rate constant of the coordinated water exchange of $AlAc^{2+}$.

The temperature dependence of the rate constants, k_{32}, gave the Arrhenius energy of activation, $\Delta E^{\ddagger}_{32}$, enthalpy of activation, $\Delta H^{\ddagger}_{32}$, and entropy of activation, $\Delta S^{\ddagger}_{32}$ (Table 3).

It is predicted that the slow relaxation effect in the present observation can be ascribed to the reaction of equilibrium 2.

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