Equilibria and Kinetics of Al(III) Complex Formation with Semi-Xylenol Orange

Sadaaki MURAKAMI*, Megumi KAGAWA* and Takashi YOSHINO*

(Received August 2, 1974)

Abstract

The equilibria and the kinetics of the Al(III) complex formation with Semi-Xylenol Orange (SXO) in an aqueous solution have been investigated potentiometrically and spectrophotometrically. Al(III) forms three complex species, $AlSXO^-$, AlHSXO and $Al(OH)SXO^{2-}$ with SXO. The stability constants and the rate constants of these complex formations have been determined. The complex formation may proceed following the Eigen-Tamm mechanism, and the dissociation of the water molecule from the aquo ion may be the rate-determining of the complex formation.

Introduction

Although there have been a number of investigations about the metal complex formations and the anayltical utilities of the sulphonphthalein indicators, the relatively meager kinetic data have been reported for these indicators[1]. This arises mainly from the lack of the pricise data of the equilbria of the complex formations of these indicators. Recently, we investigated the equilibria of these indicators and the uncertainties have been fairly cleared.

In the present study, Semi-Xylenol Orange (SXO) has been chosen as a ligand, and the first, the equilibria and then the kinetics of its complex formation with Al(III) have been investigated. The former was measured potentiometrically and the latter spectrophotometrically using the rapid-mixing technique.

Experimental

The apparatus and the experimental techniques for potentiometric and spectrophotometric investigations are the same as described earlier[2].

The procedure of the determination of the apparent rate constants of the color change ractions of Al(III)–SXO complexes is performed as follows. A solution containing SXO and buffer solution (0.1 M acetic acid and 0.1 M sodium actetate) and 1 M KNO_3 solution ($\mu=0.1$) was placed in a cell with light-pass of 1.0 cm-length. Then Al(III) in excess (*i.e.*, 10–100% excess) over SXO was rapidly added by a pipette with stirring. The absorbance of the solution at a suitable wavelength was a function of the reaction time. The measurements were done at room temperature.

---

* Department of Chemical Technology

Results

pH titration curves

Figure 1 shows the results of the pH titrations of the solutions containing Al(III) only, and Al(III) and each ligand which is SXO, IDA (iminodiacetic acid), NTA (nitrilotriacetic acid) or EDTA (ethylenediaminetetraacetic acid) at 1 : 1 molar ratio of Al(III) to each ligand.

The complex species and their formation constants were determined by the same method as described earlier²⁾, and their results are listed in table 1.

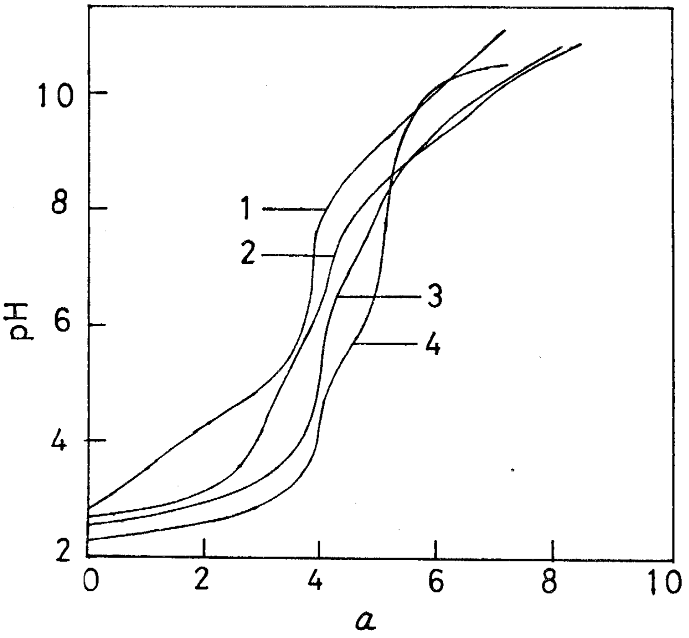

Fig. 1 Potentiometric titration curves of Al(III) complexes with following ligands at 25±0.1°C in 0.1 M KNO_3 solutions.
1–IDA, 2–NTA, 3–SXO, 4–EDTA.
a = number of moles of base added per mole of liand.
T_L: 1–1.22×10^{-3} M, 2–7.48×10^{-4} M, 3–9.92×10^{-4} M, 4–1.69×10^{-3} M.
T_{Al}: 1–1.23×10^{-3} M, 2–7.28×10^{-4} M, 3–9.99×10^{-4} M, 4–1.50×10^{-3} M.

Absorption spectra of Al(III)–SXO complexes

The SXO solutions containing Al(III) at 2 : 1 molar ratio of Al(III) to ligand at different pH values were measured spectrophotometrically by the same method as described earlier²⁾. Even in a strongly acidic solution (pH 1.5–2), the absorbance of the Al(III)–SXO solution is different from that of the SXO, indicating the formation of the complexes. With pH increasing, the absorbance shifts toward the longer wavelength, and two patterns of the absorption bands appear at pH near 5 and 7, probably corresponding to the complex species, $AlSXO^-$ and $Al(OH)SXO^{2-}$, respectively. Over pH 8, the absorbance increases rapidly and is quite similar to that of SXO at more alkaline solution, probably by the dissociation of $Al(OH)SXO^-$ to AlO_2^- ion and free ligand species. From the results of the mole-ratio method, Al(III) forms the complexes of only 1: 1 mole ratio of Al(III) to SXO. The optical constants of the main complex species determined are as follows: $AlSXO^-$: $\lambda_{max}=470$ nm; $\varepsilon=2.24\times10^4$ l.mole^{-1}.cm^{-1}, $Al(OH)SXO^{2-}$: $\lambda_{max}=487$ nm; $\varepsilon=2.36\times10^4$ l.mol^{-1}.cm^{-1}.

Apparent rate constants of the complex formations

The apparent rate constants of the color cahnge reactions of Al(III)–SXO complexes were determined as follows. From the results of the above potntiometric and spectrophotometric measurements, in order to minimize hydrolysis and polymerization of Al(III), the investigations of the apparent rate constants were performed in acidic media (pH about 3–5) by measuring the changes of the absorbances of the solutions in which the protonated and the simple complex species may be predominant.

When Al(III) concentration was at least in 10-fold excess over that of SXO, a pseudo-first-order kinetics was obayed in most cases. Pseudo-first-order rate constant k_{obs} was evaluated from the slope of such as

$$k_{obs}=-dln(D_\infty-D_t)/dt$$

where D_∞ and D_t represent the absorbances at the end of the reaction and at time t, respectively. No signifficant dependence was observed for k_{obs} on the initial concentration of SXO. Plots of the observed pseudo-first-order rate constant k_{obs} against Al(III) are not straight lines but curves as shown in Fig. 2. Assuming the one step mechanism

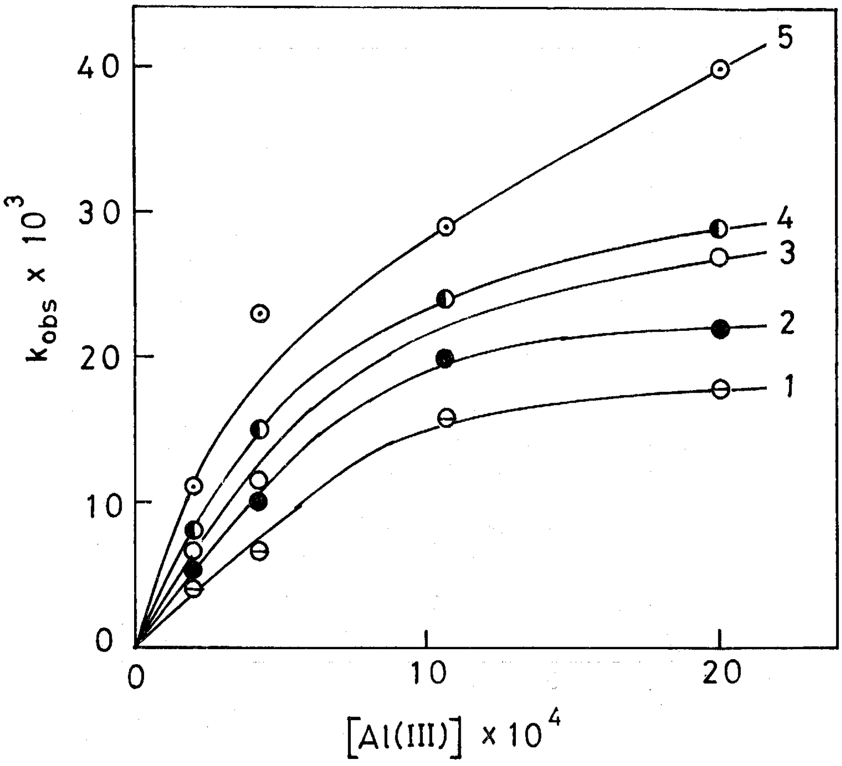

Fig. 2. Plot of k_{obs} *vs.* total concentration of Al(III) at various hydrogen ion concentrations at room temp. and $\mu=0.1$.
pH: 1–3.95, 2–4.13, 3–4.29, 4–4.46, 5–4.67.

such plots should give a straight line with a slope k_f and an intercept k_r,

$$\mathrm{Al(III)+SXO} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Al(III)SXO}$$

$$k_{\mathrm{obs}} = k_f \mathrm{Al(III)} + k_r$$

The curves can thus be interpreted in terms of the two mechanisms.

$$\mathrm{Al(III)+SXO} \overset{K_p}{\rightleftharpoons} \mathrm{Al(III)\cdots SXO}$$

$$(K_p:\quad \text{preequilibrium constant})$$

$$\mathrm{Al(III)\cdots SXO} \underset{\vec{k}}{\overset{\vec{k}}{\rightleftharpoons}} \mathrm{Al(III)SXO}$$

Since Al(III) is in large excess over SXO, and is regarded as constant during the reactions, k_{obs} can be written as a function of Al(III).

$$k_{obs} = \frac{\vec{k}\, K_p[\mathrm{Al(III)}]}{1+K_p[\mathrm{Al(III)}]} + \overleftarrow{k}$$

Figure 3 shows a linear plot of $1/(k_{\mathrm{obs}} - \overleftarrow{k})$ *versus* $1/[\mathrm{Al(III)}]$. We have for the present no evidence of the actual structure of the intermediate Al(III)···SXO; it may or may not be so called ion pair.

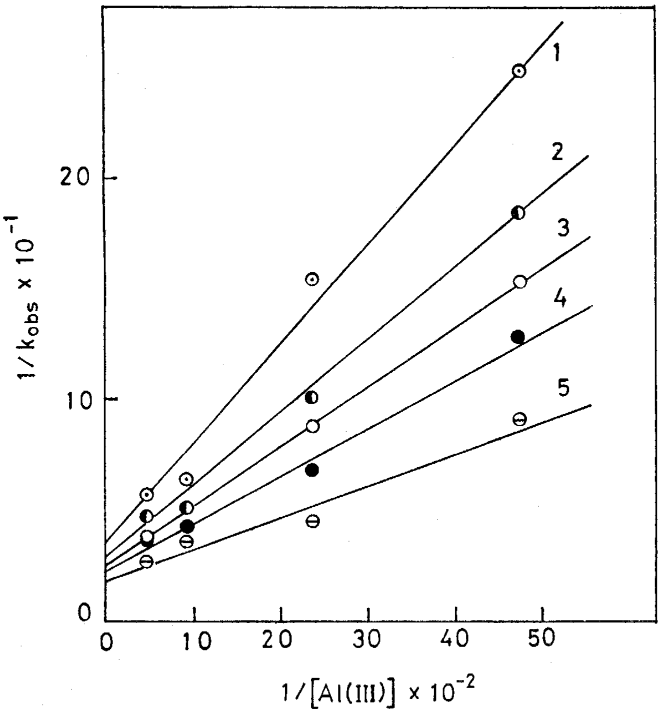

Fig. 3 Plot of $1/k_{obs}$ *vs.* inverse of the total concentration of Al(III) for Al(III)-SXO at various hydrogen ion concentrations at room temp. and $\mu=0.1$.
pH: 1–3.95, 2–4.13, 3–4.29, 4–4.46, 5–4.67.

In the present work the value of k_f for Al(III)–SXO system is discussed. It is difficult to discuss k_f, as the plots of k_{obs} *versus* [Al(III)] have intercepts almost near the origin in most cases. This is consistent with the large value of apparent stability constant $K=[\mathrm{Al(III)SXO}]/[\mathrm{Al(III)}][\mathrm{SXO}]$.

The increase of k_f with decreasing [H] is interpreted by considering the acid dissociation of aquo ions, Al(III) and SXO. Considering all possible chemical species and equilibria under the present experimental conditions, second-order rate constants are difined as follows:

$$\left\{\begin{array}{l} \mathrm{Al^{3+}+H_3SXO^-} \xrightarrow{k_{11}} \\ \mathrm{Al^{3+}+H_2SXO^{2-}} \xrightarrow{k_{12}} \end{array}\right. \qquad \left\{\begin{array}{l} \mathrm{AlOH^{2+}+H_3SXO^-} \xrightarrow{k_{21}} \\ \mathrm{AlOH^{2+}+H_2SXO^{2-}} \xrightarrow{k_{22}} \end{array}\right.$$

The proton transfer of ligand and the hydrolysis of Al(III) are known to be fast as compared to the complex formation reactions[3]. Acid dissociation constants of SXO[4] and Al(III)[5] were reported. Contributions of the charge types of the ligand species, $\mathrm{H_4SXO}$, $\mathrm{HSXO^{3-}}$ and $\mathrm{SXO^{4-}}$, and the metal ion $\mathrm{Al(OH)_2^+}$ were neglected. Following equation express k_f.

$$k_f=\{k_{11}K_aK_3[\mathrm{H}]^2+(k_{12}K_a+k_{21}K_3)[\mathrm{H}]+k_{22}\}/([\mathrm{H}]K_a+1)([\mathrm{H}]K_3+1)$$

where K_a and K_n are the acid formation constants of Al(III) and ligand respectively, $K_a=[\mathrm{Al(OH_2)_6^{3+}}]/[\mathrm{Al(OH_2)_5(OH)^{2+}}][\mathrm{H}]$ and $K_n=[\mathrm{H_nSXO^{n-4}}]/[\mathrm{H_{n-1}SXO}^{\,n-5}][\mathrm{H}]$. In Fig. 4, $k_f([\mathrm{H}]K_a+1)([\mathrm{H}]K_3+1)$ is ploted against [H] to give a straight line, where [H] was calculated directly from the observed value of pH without correction of activity coefficient.

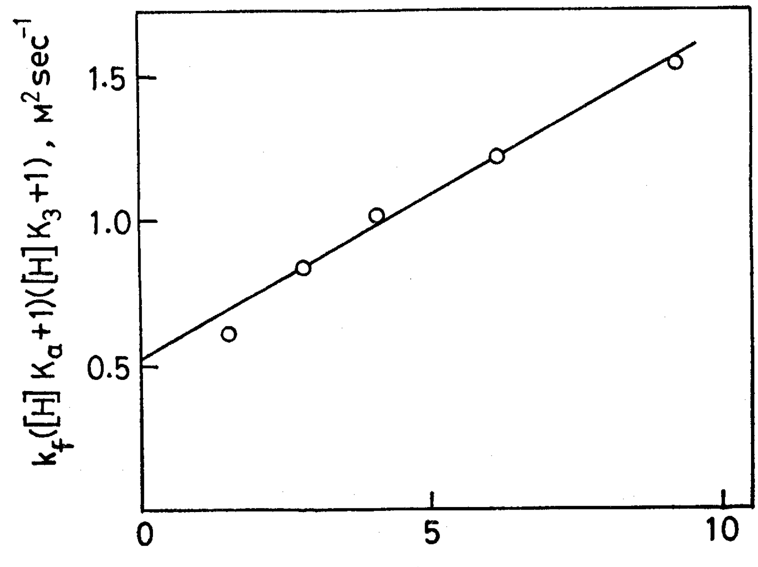

Fig. 4 Plot of $k_f([\mathrm{H}]K_a+1)([\mathrm{H}]K_3+1)$ *vs.* hydrogen ion concentration for Al(III)-SXO at room temp. and $\mu=0.1$.

The term of k_{22} correspond to the intercept, and the term of $k_{12}K_a+k_{21}K_3$ to the slope of the plots, so that the values of k_{12} and k_{21} are indistinguishable. Following values of k_{12} and k_{21} have been calculated by attributing the slope only to the term $k_{12}K_a$ and to $k_{21}K_3$ respectively: $k_{12}=2.1\times10^{-2}\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$ and $k_{21}=8.1\times10^{2}\mathrm{M}^{-1}\mathrm{sec}^{-1}$. From the intercept k_{22} is obtained as $0.52\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$.

Discussion

The stability of Al(III) complex increases with increasing the chelate ring number (IDA<NTA<EDTA). The stability of Al(III)–IDA (1: 1) complex is almost equal to that of Al(III)–SXO complex, AlHSXO, indicating that the arrangement of the monoprotonated complex of SXO would be same as that of the IDA. Iminodiacetate group of SXO may coordinate to Al(III) as to the arrangement of the complex, AlHSXO. Thus the simple complex, AlSXO^-, would be formed by coordination of oxygen of the phenolic group. As compared with the stability of Al(III) complex with quadridentate ligand, NTA, that of SXO is almost similar, and is higher than that of hexadentate ligand, EDTA. This fact indicates that Al(III) has the higher affinity for oxygen of phenolic group than that of other coordination groups of EDTA.

Table 1 Formation constants of Al(III) complexes with various ligagnds at 25±0.1°C, $\mu=0.1$ ($\mathrm{KNO_3}$).

Reaction*	Log K			
	IDA	NTA	SXO	EDTA
$\mathrm{Al+L \rightleftharpoons Al}$	8.9	10.0	16.7	16.1
$\mathrm{Al+HL \rightleftharpoons AlHL}$			9.1	
$\mathrm{H+AlL \rightleftharpoons AlHL}$			3.2	
$\mathrm{AlL+OH \rightleftharpoons Al(OH)L}$	9.6	8.8	7.2	8.3
$\mathrm{Al(OH)L+OH \rightleftharpoons AlO_2+HL}$	9.0			

* Charge of ion is omitted for simplicity.

Over about pH 8, pH curves of IDA, NTA and SXO complexes shows the same tendency. Also from the result of the absorption curve of Al(III)–SXO complex, the absorption spectrum of it is identical for that of the corresponding ligand at the same pH value above pH 8. These may be considered that the metal complexes dissociate to form $\mathrm{AlO_2^-}$ and free ligand. However, EDTA complex does not show it on pH curve. This difference may be caused by that for EDTA complex, Al(III) of six-coordinate number is completely filled with five coordinated groups of EDTA and a hydroxide ion[6], however, for the other complexes, it is not completely filled with those of the corresponding ligand and with remaining the unsubstituting $\mathrm{H_2O}$ molecules.

Table 2 show the rate at which aquo ions of Al(III), Ga(III)[1], and Tl(III)[1] combine with SXO to form each complex species. It will be difficult to discuss these apparent

Table 2 Rate constants for the complex formation.

Reaction	k, $M^{-1}sec^{-1}$		
	Al(III)[a]	Ga(III)[b]	Tl(III)[c]
$M^{3+}+H_2SXO^{2-}\longrightarrow$	2.1×10^{-2}	6.9×10^{2}	2.8×10^{5}
$MOH^{2+}+H_2SXO^{2-}\longrightarrow$	5.2×10^{-1}	1.2×10^{4}	3.1×10^{6}
$MOH^{2+}+H_3SXO^{-}\longrightarrow$	8.1×10^{2}	1.1×10^{3}	5.0×10^{6}

a: at room temp., $\mu=0.1$; *b*: at 25°C, $\mu=0.1$; c: at 25°C, $\mu=2.0$.

values precisely becaues temperatures and ionic strengths are diffeernt. However the rate for each ion is practically the same as the rate fbr water exchange for that ion, about 10–100 times slower. It is believed that the only reasonable explanation for these observations may be explained by the Eigen-Tamm mechanism7). The formation reactions proceed in two steps, the first being the formation of the aquo ion-ligand outer shere complex, followed by elimination of H_2O from the aquo ion in the same manner as in the water-exchange process. As SXO is a multidentate ligand, the complex formation process consists of several steps. The outer-shere complex must be formed first, regardless of the successive mechanism. An inner-shere coordinated water molecule is substituted by one of the coordinating groups of SXO next. The dissociation of the water molecule is the rate determining It seems probable that the first coordination to the metal occurs through one of the carboxylic group, the nitrogen of the imino group and the oxygen of the phenol or quinone which is directly connected with the π-electron system of the ligand, the intermediate must be formed before the coordination of the phenol oxygen. Then the rate-determining step which may be S_N1 or S_N2 follows and bond between the imino nitrogen and the phenolic or the quinone oxygen was expected.

The rate for the reaction of $Al(OH)(OH_2)_5^{2+}$ is higher than that of $Al(OH_2)_6^{3+}$. As pointed out in the formation of Ni(II) complexes8,9), it is understandable that the electron donation from hydroxide ion makes the dissociation of coordinated water molecules from $Al(OH)(OH_2)_5^{2+}$ faster than aquo Al(III) ion. Addition to this $Al(OH)(OH_2)_5^{2+}$ is basic and ligand H_2SXO^{2-} is acid. Thus the hydrogen bond would be formed between $AlOH^{2+}$ and H_2SXO^{2-} thereby stabilizing more effectively the $AlOH^{2+}\cdots H_2SXO^{2-}$ outer-sphere complex than the $Al(OH_2)_6^{3+}\cdots H_2SXO$ outer-sphere complex.

A similar enhancement of faster rate constant for the complex formation of $Al(OH_2)_6^{3+}$ and $Al(OH)(OH_2)_5^{2+}$ with H_3SXO^- than with H_2SXO^{2-}, can be accounted for in terms of the internal conjugate base mechanism.

The order of the values of the color change constants is, namely, Al(III) < Ga(III) < Tl(III). The order of the rate for each ion is the same as that of the water exchange for each ion. The influence of the size may be seen. With each ion the rate of the complex formation increases with increase of the size. Since M^{3+}–OH_2 bond strength should decrease with increase of size of the metal ion. This correlation suggests that the transition state for the exchange reactionis is attained by breaking an existing M^{3+}–OH_2 bond to a much greater extent than a new complex is formed, that is, mechanism is essentially dissociative.

References

1) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama and M. Fujimoto: Bull. Chem. Soc. Japan, **45**, 1417–1427 (1972)
2) T. Yoshino, S. Murakami, M. Kagawa and T. Araragi: Talanta, **21**, 79–85 (1974)
3) L. P. Hlomes, P. L. Cole and M. Eyring: J. Phys. Chem., **72**, 301–304 (1968)
4) M. Murakami, T. Yoshino and S. Harasawa: Talanta, **14**, 1293–1307 (1967)
5) R. K. Schofield and A. W. Taylor: J. Chem. Soc., 4445–4448 (1954)
6) G. Schwarzenbach: Helv. Chim. Acta, **32**, 839–853 (1949)
7) M. Eigen and K. Tamm: Z. Electrochem., **66**, 93–107 (1962)
8) S. Funahashi and M. Tanaka: Inorg. Chem., **8**, 2159–2165 (1969)
9) *Idem*: *ibid.*, **9**, 2092–2097 (1970)