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Equilibria of Aluminium(III) Complexes with 3,3′-Bis[*N,N′*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein

Sadaaki Murakami* and Takashi Yoshino

Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

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Synopsis. A potentiometric and spectrophotometric study of aluminium(III) complexes with 3,3′-bis[*N,N′*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein has been performed. Evidence was found for the formations of 1 : 1 and 2 : 1 (metal : ligand) complexes and it was assumed that protonated and hydroxo complexes are formed in addition to the simple complexes. The formation constants for these complexes were determined and suggestions are made concerning the probable structures of the complexes.

Xylenol Orange (abbreviated as XO or H_6xo) has been widely used as an indicator in chelatometric and spectrophotometric determinations of numerous metal ions.[1,2] These are also many findings concerning the solution chemistry of its metal complexes. However, most of these reports have treated bivalent metal ions,[3–6] but not trivalent ones. In a previous work,[7] the Fe(III) complexes of XO were investigated and it was found that hydroxo complexes are formed in neutral and alkaline media. With regard to Al(III), Otomo[8] pointed out that its complex formation equilibria are complicated, when he studied the spectrophotometric determination of aluminium with XO. The complexes for the Al(III) system are expected to be similar to those found in the Fe(III). This paper reports the results of a potentiometric and spectrophotometric study on the Al(III) complexes with XO.

Experimental

XO was synthesized and purified as described in reference 9. The other reagents and procedures were the same as described previously.[10,11] All the measurements were performed at 25±0.1 °C; the ionic strength of the solutions was maintained at 0.1 with sodium perchlorate.

The formation constants of the complexes were calculated in the manner described previously.[10,11] The acid formation constants of XO used in the calculations were those determined previously[9] (log k_i: 12.23, 10.56, 6.74, 2.85, 2.32, and 1.5 for $i=1$ to 6, respectively).

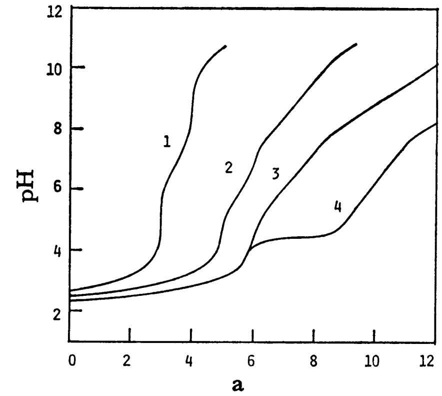


Fig. 1. Potentimetric titration curves of Al(III) and XO solutions. a=number of moles of base added per mole of XO.
1-XO, 2, 3 and 4-1/1, 2/1 and 3/1 solutions, respectively. [XO]=about 1×10^{-3} mol/l, and [Al(III)] is varied.

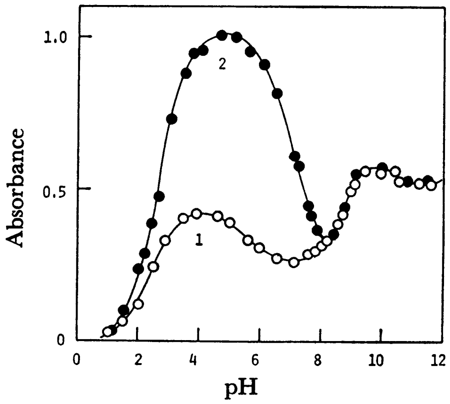


Fig. 2. Variations in the absorbances of Al(III) and XO solutions at a given wavelength as a function of pH. 1-1/1 and 2-2/1 solutions, respectively. Wavelength: 1-554 and 2-555 nm.

Results

Potentiometric titrations of XO solutions containing 1 : 1, 2 : 1, and 3 : 1 molar ratios of Al(III) to XO were performed (the molar ratios of Al(III) to XO, hereinafter, are referred to as "1/1", "2/1", and "3/1"). The results are shown in Fig. 1. The visible absorption spectra of the 1/1 and 2/1 solutions at various pH

Table 1. Formation constants, wavelengths, and absorptivities of Al (III) complexes with XO at 25 °C and $\mu=0.1$ ($NaClO_4$)

Reaction	log K	λ_{max} / nm	$\varepsilon\times10^{-4}$ / $cm^{-1}\,mol^{-1}\,l$
$Al^{3+}+Hxo^{5-}\rightleftharpoons{}^{*}AlHxo^{2-}$	16.3	554	3.67
$2Al^{3+}+xo^{6-}\rightleftharpoons{}^{*}Al_2xo$	27.0	555	8.29
$H^{+}+{}^{*}Al(OH)Hxo^{3-}\rightleftharpoons AlHxo^{2-}+H_2O$	5.8 5.6[a)]	502	3.51
$2H^{+}+{}^{*}[Al(OH)]_2xo^{2-}\rightleftharpoons Al_2xo+2H_2O$	13.4 13.1[a)]	510	3.45

*The complexes corresponding to the λ_{max} and ε values. a) Determined spectrophotometrically (the others potentiometrically).

values (pH 1—13) were measured between 350 and 700 nm. Figure 2 shows the variations in the absorbances at a given wavelength as a function of pH. The formation constant, absorptivity, and wavelength of each complex species are listed in Table 1.

Discussion

Complex Formation Equilibria. Both 1/1 and 2/1 titration curves have two inflections: at $a=5$ and 6, and at $a=6$ and 8, respectively. The 3/1 titration curve is quite the same as the 2/1 curve up to $a=6$, but beyond this a value up to 9 there is another buffer region in which aluminium(III) hydroxide was precipitated. The extent of this buffer region over three units of a indicates that there exists one mole of free Al(III) ion per mole of XO, and that not more than two Al(III) ions can combine with one XO molecule.[11] One proton in a XO molecule remains undissociated at $a=5$ for the 1/1 solution, and all available protons dissociate at $a=6$ for the 2/1 solution, indicating the formations of the complexes, $\mathrm{AlHxo^{2-}}$ and $\mathrm{Al_2xo}$, at the respective a values. The extent of the buffer region from $a=6$ to 8 for the 2/1 solution is just double that from $a=5$ to 6 for the 1/1 solution. These facts suggest that each Al(III) ion in the 1 : 1 and 2 : 1 complexes is hydrolyzed to liberate one proton from a water molecule in its inner coordination sphere.[12] Thus, the hydroxo complexes, $\mathrm{Al(OH)Hxo^{3-}}$ and $\mathrm{[Al(OH)]_2xo^{2-}}$, are assumed to be formed as found in the Fe(III) and XO system.[7]

Both 1/1 and 2/1 titration curves show a long buffer region beyond $a=6$ and $a=8$, respectively. The change in the absorbance is observed in Fig. 2 between pH 7 and 10 for the 1/1 solution and between pH 8 and 10 for the 2/1 solution. With increase in pH from 7 and from 8, each spectrum shifted to longer wavelengths (502 to 578 nm for the 1/1 solution and 510 to 578 nm for the 2/1 solution). Both 1/1 and 2/1 spectra above pH 10 were exactly the same as those of the free XO solutions. These facts suggest that the complexes, $\mathrm{Al(OH)Hxo^{3-}}$ and $\mathrm{[Al(OH)]_2xo^{2-}}$, are further hydrolyzed to dissociate into $\mathrm{Al(OH)_4^-}$ and XO in such alkaline media. In acidic media, the 1/1 and 2/1 titration curves have a long buffer region. The change in the absorbance is observed in Fig. 2 from pH 4 down to 1 for the 1/1 solution and from pH 5 to 1 for the 2/1 solution. With decrease in pH from 4 and from 5, the 1/1 and 2/1 spectrum bands at 554 and at 555 nm respectively disappeared and a new band appeared at 435 nm for both 1/1 and 2/1 solutions. Both 1/1 and 2/1 spectra around pH 1 were just the same as those of the free XO solutions. These facts suggest that the complexes, $\mathrm{AlHxo^{2-}}$ and $\mathrm{Al_2xo}$, dissociate into Al(III) aquo ion and XO in such acidic media.

Summarizing the foregoing discussion, the equilibria of complex formations for the Al(III) and XO system are as indicated in the following scheme.

The 1/1 solution:

$$\overset{\mathrm{pH}<1}{\mathrm{Al^{3+}+H_6xo}} \rightleftharpoons \overset{\mathrm{pH}\ 4}{\mathrm{AlHxo^{2-}}} \rightleftharpoons$$

$$\overset{\mathrm{pH}\ 7}{\mathrm{Al(OH)Hxo^{3-}}} \rightleftharpoons \overset{\mathrm{pH}>10}{\mathrm{Al(OH)_4^-+H_2xo^{2-}}}.$$

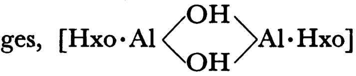
The 2/1 solution:

$$\overset{\mathrm{pH}<1}{\mathrm{2Al^{3+}+H_6xo}} \rightleftharpoons \overset{\mathrm{pH}\ 5}{\mathrm{Al_2xo}} \rightleftharpoons$$

$$\overset{\mathrm{pH}\ 8}{\mathrm{[Al(OH)]_2xo^{2-}}} \rightleftharpoons \overset{\mathrm{pH}>10}{\mathrm{2Al(OH)_4^-+H_2xo^{4-}}},$$

where each pH value indicates that the corresponding species is predominant in the solution around this pH value.

Complex Structures. The XO molecule has two chelating groups on each side of its large sulfonphthalein nucleus; each chelating group reacts with metal ion independently of each other.[2] Thus, the proton of the 1 : 1 complexes, $\mathrm{AlHxo^{2-}}$ and $\mathrm{Al(OH)Hxo^{3-}}$, may be the one which attaches to the amino nitrogen of another bis(carboxymethyl)aminomethyl group which is not coordinating to an Al(III) ion, because the amino nitrogen may dissociate the proton in more alkaline media.[9]

With regard to the 1 : 1 hydroxo complex, $\mathrm{Al(OH)Hxo^{3-}}$, there is some possibility of a dimerized structure with hydroxo bridges,  $\mathrm{[Hxo{\cdot}Al\overset{OH}{\underset{OH}{\diamond}}Al{\cdot}Hxo]^{6-}}$, as discussed for $\mathrm{Al(OH)sxo^{2-}}$ [12] and $\mathrm{Fe(OH)Hxo^{3-}}$.[7] A polynuclear complex[13,14] is possible for the 2 : 1 hydroxo complex, $\mathrm{[Al(OH)]_2xo^{2-}}$, as a result of hydrolysis of two Al(III) ions attached to either side of the sulfonphthalein nucleus,  $\mathrm{[\,\underset{HO}{>}Al{\cdot}XO{\cdot}Al\overset{OH}{<}\,]_n^{2n-}}$ ($n\gg2$), as discussed for $\mathrm{[Fe(OH)]_2xo^{2-}}$.[7] However, a complete discussion of the structures for these hydroxo complexes must await further investigation.

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