

# Equilibrium Study on the Characteristic Color-Changing Reaction of Lanthanum Complex of 3-[[Bis(carboxymethyl)amino]methyl]-1,2-dihydroxyanthraquinone (Alizarin Complexon) with Fluoride Ion

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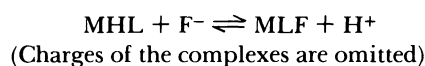
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(Received April 25, 1988)

Complexation equilibria between lanthanum (M), 3-[[bis(carboxymethyl)amino]methyl]-1,2-dihydroxyanthraquinone (Alizarin Complexon,  $H_4L$ ) and fluoride were studied by potentiometry with fluoride ion selective electrodes and by spectrophotometry.  $M_2HL_2$  and a further protonated species react with fluoride to form  $M_2HL_2F$  and  $M_2H_2L_2F$ , whereas  $M_2L_2$  does not. The unexpectedly large stability constant of  $10^{4.12}$  for the reaction,  $M_2HL_2 + F^- \rightleftharpoons M_2HL_2F$ , may be ascribed to the incorporation of fluoride ion in a specially organized core of  $M_2HL_2$ .

Rare earth metal (M) complexes of alizarin complexon(3-[[bis(carboxymethyl)amino]methyl]-1,2-dihydroxyanthraquinone; ALC or  $H_4L$ ; Fig. 1) react with fluoride ion to show a characteristic color change from red to blue.<sup>1)</sup> This reaction provides the selective and sensitive photometric method for fluoride.<sup>2)</sup> Various modifications of this reaction have been proposed to overcome the disadvantages of large reagent blank, slow attainment of equilibria and insufficient affinities toward fluoride.<sup>3)</sup> In contrast to abundance of conventional bleaching methods which utilize the dissociation of a color-forming reagent from the metal complex by the reaction with fluoride ion, no other reaction systems involving the formation of the mixed ligand complex have been found except those with the derivatives.<sup>4–6)</sup>

Although several attempts have been made to elucidate the mechanism of this color development, they are not sufficient.<sup>10–13)</sup> From the similarity of the absorption spectrum of the blue species to that of completely deprotonated ALC, the following equation was first proposed by Leonard and West.<sup>10)</sup>



Formation of the mixed ligand complex, MLF, by displacement of one of the water molecules with fluoride was supposed to promote the dissociation of the last proton on ALC, causing the color change. Later on, rather complicated formulas such as  $M_5L_4F_4$ ,<sup>11)</sup>  $M_2H_2L_2F_2$ ,<sup>12)</sup> and  $M_5L_4F_2$ <sup>13)</sup> have been proposed as the composition of the mixed ligand complexes. Various molar ratio methods used in these

studies were not suited for the system, because ALC has so many functional groups that various species can be formed in a successive manner as in the case of Xylenol Orange,<sup>14)</sup> and because affinity to fluoride is too low to give a well-defined break point on the plots.

We have made systematic studies on the formation of mixed ligand complexes with fluoride and simpler ligands,<sup>15–17)</sup> using fluoride ion-selective electrodes. The same approach is applied to this system.

## Experimental

**Reagents.** Lanthanum solution was prepared from the nitrate hexahydrate and was standardized against  $Na_2H_2edta$ . Potassium fluoride was dried in a platinum crucible for 24 hours at 110 °C. Fluoride solutions were stored in polyethylene containers. Potassium nitrate was recrystallized twice. Carbonate-free potassium hydroxide solution was prepared as described elsewhere.<sup>18)</sup>

ALC ( $H_4L \cdot 2H_2O$ ) was prepared and purified as described in literature.<sup>19,20)</sup> Purity of the reagent was confirmed by elemental analysis and potentiometric titration. It was dissolved in known amounts of carbonate-free potassium hydroxide solution. Acetate buffer has been used for the earlier equilibrium studies of this system by photometry.<sup>10–12)</sup> As the buffer proved to alter the equilibria,<sup>21)</sup> no buffer was used in this study except 2-morpholino-1-propanesulfonic acid.

**Measurement.** Details of the potentiometry were the same as described previously.<sup>14–16)</sup> Visible absorption spectra were recorded with a UNION high-sens spectrophotometer SM-401 and a Shimadzu UV-250.

## Results

**Protonation Equilibria of ALC.** Solutions containing 3 to  $9 \times 10^{-3}$  mol  $dm^{-3}$  ALC were potentiometrically titrated with a nitric acid or a potassium hydroxide solution between  $-\log[H^+]$  3 and 8. At lower  $-\log[H^+]$  the reagent precipitated as  $H_4L$ , the solubility of which has been reported to be  $5 \times 10^{-4}$  mol  $dm^{-3}$ .<sup>20)</sup> The average number of protons bound to the ligand,  $\bar{n}_H$  was calculated by

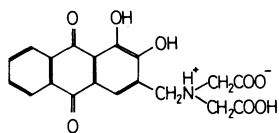


Fig. 1. Structure of ALC.

$$\bar{n}_{H,o} = \frac{4C_L + C_H - C_{OH} - [H^+] + [OH^-]}{C_L}, \quad (1)$$

where  $C_L$ ,  $C_H$ , and  $C_{OH}$  are the analytical concentrations of the ligand, hydrogen, and hydroxide ions added, respectively (Fig. 2). The third and fourth protonation constants were determined by the conventional method.

Visible absorption spectra were recorded for the solutions containing  $1 \times 10^{-4}$  mol dm $^{-3}$  ALC at various  $-\log[H^+]$  values between 2.0 and 7.1. A distinct isosbestic point was observed at 455 nm. The third protonation constant was determined by fitting a set of normalized curves to the plot of the absorbance change at 540 nm (squares in Fig. 3).

The constants obtained are as follows:  $\log K_3=5.58$  by potentiometry, and 5.52 by spectrophotometry;  $\log K_4=2.48$  by potentiometry. These are in good agreement with those in literature:  $\log K_3=5.47^{13}$  and  $5.54^{22}$ ;  $\log K_4=2.54^{13}$  and  $2.40^{22}$ .

**Complexation Equilibria of Lanthanum Ion with ALC.** Complexation equilibria between lanthanum

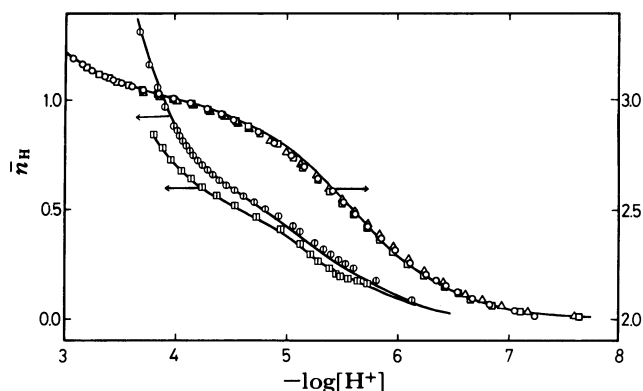


Fig. 2. Plots of  $\bar{n}_H$  vs.  $-\log[H^+]$  for the  $\text{La}^{3+}$ -ALC system (25°C, 0.1 mol dm $^{-3}$   $\text{KNO}_3$ ).  $C_M/10^{-3}$  mol dm $^{-3}$ : (○, □, △) 0; (⊙) 0.19; (⊞) 0.51.  $C_L/10^{-3}$  mol dm $^{-3}$ : (○) 4.8; (□) 6.7; (△) 8.6; (⊙) 0.20; (⊞) 0.52. The solid lines are calculated with the constants obtained.

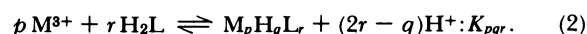
Table 1. Average Deviation of  $\bar{n}_H$  for Various Combination of Species in La-ALC System

| No. | Species considered |                                  |                         |    |                        | $\Delta\bar{n}_H^a$ |
|-----|--------------------|----------------------------------|-------------------------|----|------------------------|---------------------|
|     | MHL                | $\text{M}_2\text{H}_2\text{L}_2$ | $\text{M}_2\text{HL}_2$ | ML | $\text{M}_2\text{L}_2$ |                     |
| 1   | ○                  | ×                                | ×                       | ○  | ×                      | 0.090               |
| 2   | ○                  | ×                                | ×                       | ×  | ○                      | 0.153               |
| 3   | ○                  | ×                                | ○                       | ○  | ×                      | 0.021               |
| ④   | ○                  | ×                                | ○                       | ×  | ○                      | 0.010               |
| 5   | ×                  | ×                                | ○                       | ○  | ×                      | 0.045               |
| 6   | ×                  | ×                                | ○                       | ×  | ○                      | 0.023               |
| 7   | ×                  | ○                                | ○                       | ○  | ×                      | 0.031               |
| ⑧   | ×                  | ○                                | ○                       | ×  | ○                      | 0.015               |
| 9   | ×                  | ○                                | ×                       | ○  | ×                      | 0.162               |
| 10  | ×                  | ○                                | ×                       | ×  | ○                      | 0.225               |

a)  $\Delta\bar{n}_H = (\sum(\bar{n}_{H,c} - \bar{n}_{H,o})^2 / N)^{1/2}$ ;  $N$ : number of data.

ion and ALC were potentiometrically studied. Preliminary experiments showed that addition of excess lanthanum ion over ALC causes precipitation of complexes at any  $-\log[H^+]$  and that even in the presence of excess ALC precipitation occurs at lower  $-\log[H^+]$ . Thus,  $0.2$  to  $1 \times 10^{-3}$  mol dm $^{-3}$  solutions containing lanthanum ion and a slight excess of ALC were subjected to potentiometry. The  $\bar{n}_H$  value was likewise calculated by Eq. 1 and is shown as a function of  $-\log[H^+]$  in Fig. 2. The plateau at  $\bar{n}_H$  equal to 0.5 suggests the presence of polynuclear species.

The complexation equilibria are generally expressed by



Then  $\bar{n}_H$  is given by

$$\bar{n}_{H,c} = \frac{\sum \sum \sum q [\text{M}_p\text{H}_q\text{L}_r]}{C_L}. \quad (3)$$

Various combinations of the possible complexes were assumed and  $K_{pqr}$  values in each set were refined to give a minimum error square sum about  $\bar{n}_H$ 's expressed by Eqs. 1 and 3 (Table 1). Both the combinations of species, Nos. 4 and 8 gave satisfactory agreement. Formation of  $\text{M}_2\text{L}_2$  and  $\text{M}_2\text{HL}_2$  is definite, whereas the composition of the other species present at lower  $-\log[H^+]$  region could not be determined whether MHL or  $\text{M}_2\text{H}_2\text{L}_2$ , since  $\Delta\bar{n}_H$  did not differ so much between Nos. 4 and 8. The constants obtained are summarized in Table 2.

These equilibria were also studied spectrophotometrically with the solutions containing  $0.1 \times 10^{-3}$  mol dm $^{-3}$   $\text{La}^{3+}$  and a small excess of ALC at  $-\log[H^+]$  between 2 and 8 (Fig. 4). Spectral change between  $-\log[H^+]$  2–4 with an isosbestic point at 453 nm corresponds to the formation of  $\text{M}_2\text{HL}_2$ , whereas that between  $-\log[H^+]$  6–8 with an isosbestic point at

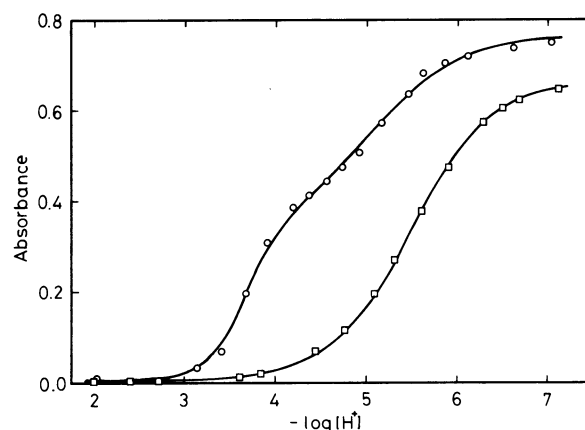


Fig. 3. Absorbance change of ALC as a function of  $-\log[H^+]$  in the presence and absence of  $\text{La}^{3+}$  (25°C, 0.1 mol dm $^{-3}$   $\text{KNO}_3$ ). Wavelength, 540 nm.  $C_M$ : (□) 0; (○)  $9.4 \times 10^{-5}$  mol dm $^{-3}$ .  $C_L$ : (□, ○)  $9.5 \times 10^{-5}$  mol dm $^{-3}$ . The solid lines are calculated with the constants obtained.

Table 2. Stability Constants for the Species Found in La-ALC and La-ALC-F Systems at 25°C and at 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>

| Equilibrium   | Equilibrium constant    |
|---|-------------------------|
| A. La-ALC system <sup>a)</sup>                          |                         |
| $2M + 2H_2L \rightleftharpoons M_2L_2 + 4H^+$           | $\log K_{202} = 0.28$   |
| $2M + 2H_2L \rightleftharpoons M_2HL_2 + 3H^+$          | $\log K_{212} = 5.58$   |
| B. La-ALC-F system                                      |                         |
| $2M + 2H_2L + F^- \rightleftharpoons M_2HL_2F + 3H^+$   | $\log K_{2121} = 9.70$  |
| $2M + 2H_2L + F^- \rightleftharpoons M_2H_2L_2F + 2H^+$ | $\log K_{2221} = 14.17$ |

a) In more acidic medium, the third species was found (see text for details).

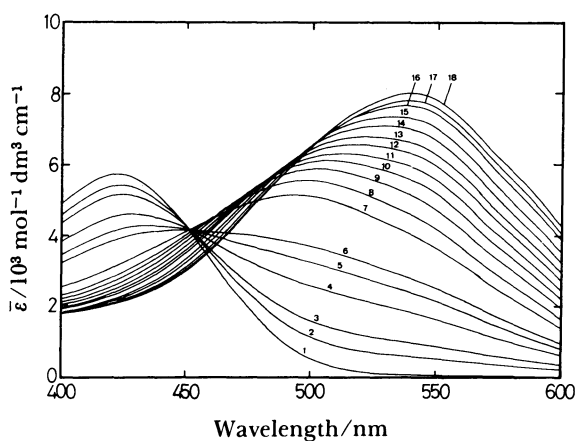


Fig. 4. Absorption spectra of La-ALC system at various  $-\log[H^+]$  (25°C, 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>).  $C_M = 9.4 \times 10^{-5}$  mol dm<sup>-3</sup>;  $C_L = 9.5 \times 10^{-5}$  mol dm<sup>-3</sup>.  $-\log[H^+]$ : (1) 2.014; (2) 3.359; (3) 3.495; (4) 3.651; (5) 3.760; (6) 3.846; (7) 4.196; (8) 4.392; (9) 4.457; (10) 4.740; (11) 4.920; (12) 5.116; (13) 5.275; (14) 5.481; (15) 5.638; (16) 5.838; (17) 6.046; (18) 7.075.

505 nm to the deprotonation of  $M_2HL_2$  to form  $M_2L_2$ . At intermediate  $-\log[H^+]$ , both reactions are concerned in the spectral change. The change in absorbance at 540 nm is shown as a function of  $-\log[H^+]$  in Fig. 3. By using the constants potentiometrically obtained and refining the molar absorptivities for  $M_2HL_2$  and MHL or  $M_2H_2L_2$ , this curve could be reproduced as shown by the solid curve in Fig. 3.

**Mixed Ligand Complexes of La-ALC with Fluoride.** The distribution of each species in the solution of  $C_M = 0.5 \times 10^{-3}$  and  $C_L = 0.55 \times 10^{-3}$  mol dm<sup>-3</sup> was calculated with the constants obtained above, and was shown as a function of  $-\log[H^+]$  in Fig. 5(a). A minor species formed in acidic media was assumed to be MHL. Even if  $M_2H_2L_2$  was assumed instead of MHL, distribution of other species was practically the same. The reaction of these species with fluoride was examined at various  $-\log[H^+]$  values indicated by arrows in Fig. 5(a). It took 30 min for equilibration at  $-\log[H^+]$  4, whereas 2 h at 5.5. Thus all the solutions were subjected to measurements after 3 h.

With the  $-\log[H^+]$  and  $-\log[F^-]$  values for each experimental point, the average number of fluoride

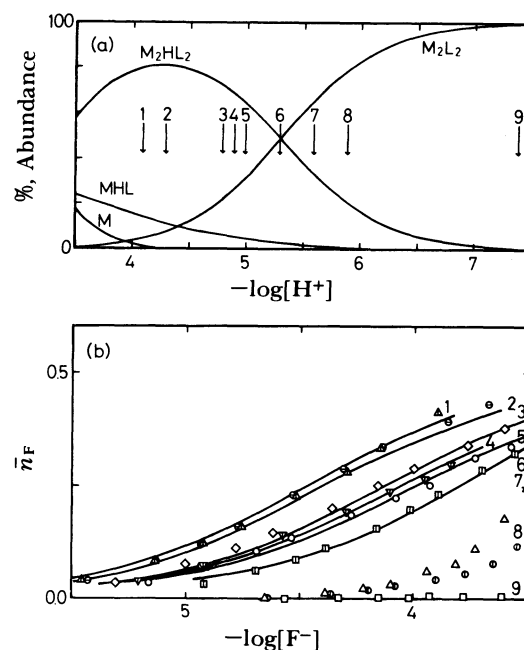


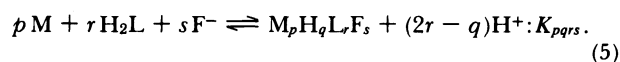
Fig. 5. (a) Distribution of species for the La-ALC system.  $C_M = 0.5 \times 10^{-3}$  mol dm<sup>-3</sup>;  $C_L = 0.55 \times 10^{-3}$  mol dm<sup>-3</sup>. MHL is arbitrarily taken as a minor species formed in acidic media (see text for details). The numbers in (a) correspond to the experimental conditions in (b). (b)  $\bar{n}_F$  vs.  $-\log[F^-]$  for the La-ALC-F system. The solid lines are calculated with the constants obtained.

ions bound to lanthanum complexes,  $\bar{n}_F$  was calculated by

$$\bar{n}_{F,0} = \frac{C_F - [F^-] - [HF] - 2[HF_2^-]}{C_M} \quad (4)$$

and is shown as a function of  $-\log[F^-]$  in Fig. 5(b). No increase in  $\bar{n}_F$  at higher  $-\log[H^+]$  indicates that  $M_2L_2$  does not react with fluoride ion. At lower  $-\log[H^+]$ , on the other hand, the curves well fit a normalized curve,  $X = \log x$ ;  $Y = 0.5x/(1+x)$ . This suggests the formation of polynuclear species.

Formation of a mixed ligand complex is expressed by



Then  $\bar{n}_F$  is given by

Table 3. Average Deviation of  $\bar{n}_F$  for Various Combination of Species in La-ALC-F System

| No. | Species considered |                                  |  |   | $\Delta\bar{n}_F^a$ |
|-----|--------------------|----------------------------------|--|---|---------------------|
|     | MHLF               | M <sub>2</sub> HL <sub>2</sub> F | M <sub>2</sub> H <sub>2</sub> L <sub>2</sub> F | M <sub>4</sub> H <sub>3</sub> L <sub>4</sub> F <sub>2</sub> |                     |
| 1   | ○                  | ×                                | ×  | ×   | 0.069               |
| 2   | ×                  | ○                                | ×  | ×   | 0.039               |
| 3   | ×                  | ×                                | ○  | ×   | 0.057               |
| 4   | ×                  | ×                                | ×  | ○   | 0.039               |
| 5   | ○                  | ○                                | ×  | ×   | 0.033               |
| ⑥   | ×                  | ○                                | ○  | ×   | 0.015               |

a)  $\Delta\bar{n}_F = (\sum(\bar{n}_{F,o} - \bar{n}_{F,c})^2 / N)^{1/2}$ ; N: number of data.

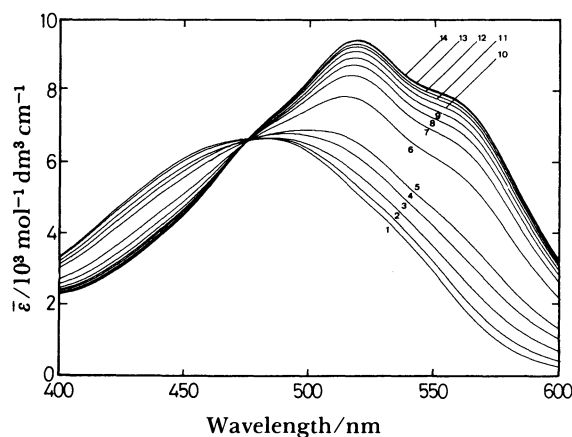
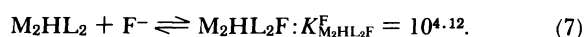


Fig. 6. Absorption spectra of La-ALC-F system at various fluoride concentrations (25°C, 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>).  $C_M = 9.3 \times 10^{-5}$  mol dm<sup>-3</sup>;  $C_L = 9.5 \times 10^{-5}$  mol dm<sup>-3</sup>;  $-\log[H^+] = 5.10$ .  $C_F / 10^{-5}$  mol dm<sup>-3</sup>: (1) 0; (2) 1.05; (3) 2.09; (4) 3.14; (5) 4.19; (6) 8.38; (7) 12.6; (8) 16.8; (9) 21.0; (10) 26.2; (11) 31.4; (12) 41.9; (13) 52.4; (14) 105.

$$\bar{n}_{F,c} = \frac{\sum \sum \sum \sum s [M_p H_q L_r F_s]}{C_M} \quad (6)$$

Various combinations of the possible mixed ligand complexes were assumed and  $K_{pqrs}$  values in each set were refined to give a minimum error square sum about  $\bar{n}_F$ 's expressed by Eqs. 4 and 6 (Table 3). Only the combination of species, No. 6 gave satisfactory agreement. Stability constants of M<sub>2</sub>H<sub>2</sub>L<sub>2</sub>F and M<sub>2</sub>HL<sub>2</sub>F were summarized in Table 2. The constant for the latter species can be recalculated as



Visible absorption spectra of La-ALC solutions were recorded in the presence of various amounts of fluoride. Figure 6 shows the results at  $-\log[H^+] = 5.10$ . The spectra of the mixed ligand complexes measured in the presence of appropriate amounts of fluoride varied with  $-\log[H^+]$ . This agrees with the presence of two mixed ligand complexes deduced above. Absorbance at 620 nm was plotted against molar ratio of fluoride to lanthanum,  $C_F/C_M$  (Fig. 7). By using the constants obtained and refining the molar absorptivi-

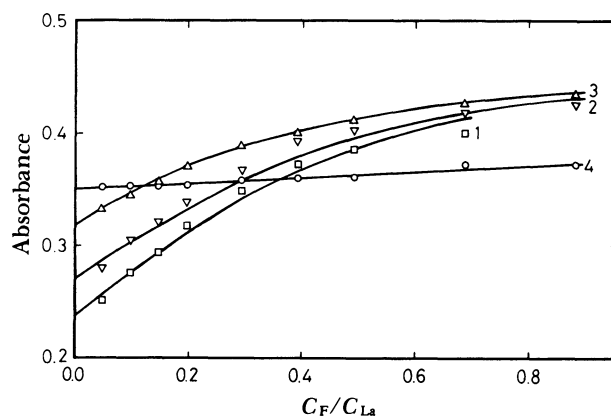


Fig. 7. Absorbance change by the addition of fluoride to La-ALC.  $C_M = 0.5 \times 10^{-3}$  mol dm<sup>-3</sup>;  $C_L = 0.55 \times 10^{-3}$  mol dm<sup>-3</sup>. Wavelength, 620 nm; pathlength, 1 mm.  $-\log[H^+]$ : (1) 4.3; (2) 4.8; (3) 5.3; (4) 5.9.

ties, the change could be reproduced as shown by the solid curves.

## Discussion

**La-ALC Complexes.** The La-ALC species formed at pH 4.6 was first considered to be MHL from the similarity of the absorption spectrum to that of H<sub>2</sub>L.<sup>10</sup> Langmyhr et. al. later pointed out the presence of another minor species at higher pH (5.5 or 6.5) from the results of continuous variation method.<sup>12</sup> Anfält and Jagner obtained the  $\bar{n}_H$  value of 0.56 in their potentiometric titration of ALC with La<sup>3+</sup> at constant pH of 4.5, and deduced that MHL and another species coexisted.<sup>13</sup>

In this study, similar values for  $\bar{n}_H$  were obtained under the same conditions, but are ascribed to only one species, M<sub>2</sub>HL<sub>2</sub> from the detailed analysis of the equilibria. In alkaline media, this species releases the proton to form M<sub>2</sub>L<sub>2</sub> ( $\log K_{M_2HL_2}^H = 5.30$ ). ALC has several donor atoms which cannot coordinate to one metal ion at the same time. The ligand in a 1:1 complex still keeps the coordination ability. On the other hand, La in a 1:1 complex is coordination-unsaturated and can interact with other donor atoms. Thus polynuclear species such as M<sub>2</sub>HL<sub>2</sub> and M<sub>2</sub>L<sub>2</sub> are formed.

**Mixed Ligand Complexes.** Anfält and Jagner

concluded, from their potentiometric data, that no protons were left on the mixed ligand complex.<sup>13</sup> If it were the case, the reactivity of La-ALC complex to fluoride would increase with pH. As shown in Figs. 5 and 7, however, the reverse trend is observed. This is just explained by that protonated species such as  $M_2HL_2$  and MHL or  $M_2H_2L_2$  do have affinities for fluoride to form  $M_2HL_2F$  and  $M_2H_2L_2F$ , whereas completely deprotonated species does not.

In a previous paper, we made a systematic study on the formation of the mixed ligand complexes with fluoride.<sup>16</sup> Reactivity of a metal ion with fluoride generally decreases by the coordination of another ligand: for example,  $K_{LaF}^F$  is  $10^{2.69}$ , whereas  $K_{LaLF}^F$  is  $10^{2.0}$  for nta<sup>3-</sup> as L,  $10^{1.7}$  for hedta<sup>3-</sup>,  $10^{1.4}$  for edta<sup>4-</sup>, and  $10^{1.8}$  for cdta<sup>4-</sup>. Compared to these values, La-ALC complexes have unexpectedly high affinities (Eq. 7), which can be ascribed to the incorporation of fluoride ion in a specially organized core of  $M_2HL_2$ . The structure is not certain at this stage.

**Analytical Implication.** The optimum pH for the determination of fluoride has empirically been determined to be around 4.3. This agrees with that of maximum proportion of  $M_2HL_2$  as shown in Fig. 5(a). At lower pH the complex dissociates, whereas at higher pH it becomes  $M_2L_2$  unreactive to fluoride ion.

Even at the optimum pH, calibration curve is straight only in lower fluoride concentration range (Fig. 7), because the conditional stability constant is not high enough. Thus large excess of the La-ALC reagent is essential.

The authors wish to thank the Grant-in-Aid for Scientific Research No. 61127007 from the Ministry of Education, Science and Culture.

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