Potentiometric Studies On Mixed Ligand Complexes

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Potentiometric evidences have been cited for the formation of 1:1:1, ternary complexes in the systems La(III)-NTA-Hydroxy acids (where hydroxy acids = malic, tartaric, 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids).

A survey of the literature revealed that very little work has so far been reported on the ternary complexes of rare earth metals. Very recently, SHARMA and TANDON¹ have studied the mixed systems, 1:1:1, La(III)-NTA-dicarboxylic acids. However, in the present communication, potentiometric studies of the mixed systems, La(III)-NTA-hydroxy acids have been described and the formation of 1:1:1 mixed complexes has been shown.

Experimental

Materials and solutions

All the chemicals used were of AR BDH grade. Lanthanum nitrate solution was prepared by dissolving AR lanthanum oxide (supplied by BARC, India) in minimum quantity of nitric acid. It was then standardised by titrating against the standard permanganate solution². Dipotassium salt of nitrilotriacetic acid was prepared by dissolving the calculated amount of the acid in the required volume of 0.1 M KOH. The standard solutions of 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids were prepared by boiling their calculated amounts with the requisite quantity of potassium bicarbonate in doubly distilled water. Solutions of malic and tartaric acids were prepared in double distilled water by direct weighing. The ionic strength (μ = 0.1) of the reaction mixture was kept constant with the help of 0.1 M potassium nitrate and the volume was always kept as 50 ml. All the solutions were kept well stoppered.

Instrument and method

The pH titrations were carried out by Phillips pH meter (PR 9404) at 32 ± 0.2°C. The pH meter was first standardised against 0.05 M potassium hydrogenphthalate (pH = 4) before the start of each titration. The following sets of different systems in duplicate were titrated against 0.1 M KOH.

System 1 La(III)NTA-malic acid

1. 10 ml (0.025 M) lanthanum nitrate (curve a).
2. 10 ml (0.025 M) dipotassium nitrilotriacetate (curve b).
3. 10 ml (0.025 M) lanthanum nitrate in presence of 10 ml (0.025 M) dipotassium nitrilotriacetate (La(III)-NTA, 1:1) (curve c).
4. 10 ml (0.025 M) malic acid (curve d).
5. 10 ml (0.025 M) lanthanum nitrate in presence of 10 ml (0.025 M) malic acid (La(III)-malic acid, 1:1) (curve e).
6. 10 ml (0.025 M) lanthanum nitrate in presence of 10 ml (0.025 M) dipotassium nitrilotriacetate and 10 ml (0.025 M) malic acid (La(III)-NTA-malic acid, 1:1:1) (curve f).

Similar sets of systems with other hydroxy acids were prepared and titrated (Figs. 2, 3 and 4).

Results and Discussion

Curve a (Figs. 1—4) represents the potentiometric titration of lanthanum nitrate giving a sharp inflection³ at m = 2.6 (m = mole of alkali added per mole of metal atom).

Fig. 1. Potentiometric titrations of La(III)-NTA-malic acid system. a = La(III), b = NTA, c = La(III)-NTA, (1:1), d = malic acid, e = La(III)-malic acid, (1:1), f = La(III)-NTA-malic acid, (1:1:1), T = Theoretical composite curve, ⇒ = precipitation.
at $m \approx 1$ (pH $\approx 10.7$) can be attributed to the titration of the proton of the acid.

Curve c (Figs. 1–4) represents the potentiometric titration of the binary mixture of 1:1, La(III)-NTA and gives two inflections. The lower one at $m = 1$ (pH $\approx 7.5$) can be correlated to the protonic titration of NTA resulting in the formation of 1:1, La(III)-NTA complex. Another weak inflection at $m \approx 2$ (pH $\approx 10$) corresponds to the formation of 1:1, La(III)-NTA monohydroxo complex as shown below:

\[
\begin{align*}
(i) \quad & \text{CH}_2\text{COO}^- + \text{H}_2\text{COO}^- + \text{La}^{3+} + \text{OH}^- \rightarrow \text{La}^{3+} \text{CH}_2\text{COO}^- \text{CH}_2\text{COO}^- \\
(ii) \quad & \text{N} \text{CH}_2\text{COO}^- + \text{OH}^- \rightarrow \text{La}^{3+} \text{CH}_2\text{COO}^- \text{CH}_2\text{COO}^-
\end{align*}
\]

Curve d (Figs. 1 and 2) represents the titration of the hydroxy acid and the sharp inflection at $m = 2$ corresponds to the simultaneous titration of both the carboxylic protons of the acid.

Curve d (Figs. 3 and 4) can be attributed to the titration of the 1-hydroxy 2-potassium naphthoate and 2-hydroxy 3-potassium naphthoate and it shows that the phenolic hydrogen of the acid is not titrable even at high pH.
Curve e (Figs. 1 and 2) represents the titration of the binary mixture of 1:1, La(III)-hydroxy acid. The first sharp inflection at m = 2 can be correlated to the formation of 1:1, La(III)-hydroxy acid complex. The second weak inflection at m ≈ 3 in the case of malic acid (Fig. 1) is due to the titration of the hydroxyl hydrogen of the acid resulting in the precipitation of 1:1, La(III)-malic acid complex as shown below:

\[
\text{HC—COOH + La}^{3+} + 2\text{OH}^{-} \rightarrow \text{HC—COO}^- \text{La}^{3+} + 2\text{H}_{2}\text{O}
\]

In the case of tartaric acid one more inflection at m ≈ 3.5 (Fig. 2) is probably due to the disproportion of the initially formed 1:1, La(III)-tartaric acid complex into 1:2, La(III)-tartaric acid complex with the simultaneous precipitation of the remaining lanthanum as hydroxide at m > 2 as indicated below:

\[
\text{HC(OH)COOH + La}^{3+} + 2\text{OH}^{-} \rightarrow \text{HC(OH)COO}^- \text{La}^{3+} + 2\text{H}_{2}\text{O}
\]

An inflection at m ≈ 2 can be due to the titration of the free lanthanum ions resulting in the precipitation of lanthanum hydroxide.

Curve f (Figs. 1 and 2) represents the titration of the ternary mixture of 1:1:1, La(III)-NTA-hydroxy acid. In both these cases, two inflections are obtained. The ill-defined inflection at m ≈ 2 corresponds to the simultaneous titration of both the protons of the carboxylic groups resulting in the formation of 1:1, La(III)-hydroxy acid complex at low pH. Another well-defined inflection at m = 3 (Figs. 1 and 2) can be due to the protonic titration of dipotassium nitrolotriacetate and resulting in the formation of 1:1:1, La(III)-NTA-hydroxy acid ternary complex at high pH. The curve f almost overlaps the curve up to m ≈ 2 in the initial stage of the titration and further supports the formation of 1:1, La(III)-hydroxy acid complex in the initial stage. In the case of tartaric acid the stepwise ternary complex formation may be as given below:

\[
\text{HC—COOH + Na}^{+} + \text{La}^{3+} + 2\text{OH}^{-} \rightarrow \left[\text{HC—COO}^- \text{La}^{3+} \right] + \text{Na}^{+} + 2\text{H}_{2}\text{O}
\]

Curve e (Figs. 3 and 4) represents the titration of the binary mixture of 1:1, La(III)-1-hydroxy 2-potassium naphthoate and 1:1, La(III)-2-hydroxy 3-potassium naphthoate. In both the cases, the formation of a white precipitate in the beginning probably indicates the formation of 1:3, La(III)-hydroxy acid complex as reported by Agrawal and Mehrotra in the case of beryllium.
Further, a sharp inflection at m = 1 can be due to the formation of the 1:1:1, La(III)-NTA-hydroxy acid complex as indicated below:

The formation of the ternary species is further supported by the dissolution of the initially formed complex at m = 1 (pH ≈ 8) and the overlapping of the curve f with the curve c beyond m = 1.

In general, 1 : 1 : 1, La(III) - NTA-hydroxy acid ternary complex formation in all the systems studied is indicated by the following facts:

(i) The lowering of curve f for the mixed complex in comparison to the curves c and d.
(ii) Absence of any precipitate during the titration of the mixed systems.
(iii) The non-super imposable nature of the theoretical composite curve T in the region of mixed complex formation (drawn by adding the horizontal distance of the curve for secondary ligand (NTA) to the horizontal distance of the curve for 1:1, La(III)-hydroxy acid system at the same pH) with the experimental curve f for the mixed system.

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1 R. C. Sharma and J. P. Tandon, communicated.
2 I. M. Kolthoff and R. Elmquist, J. Amer. chem. Soc. 53, 1225, 1232 [1931].