Stability Constants of Lactate Complexes of Lanthanides(III)

NIRADA K MOHANTY

Department of Chemistry, Ispat College, Rourkela

and

R K PATNAIK*

Department of Chemistry, Regional Engineering College, Rourkela
769 008

Lanthanides(III) form 1:1 and 1:2 complexes with lactic acid in aqueous medium. The cationic complexes formed at lower pH values dissociate at higher pH values. The equilibrium constants of the reactions have been calculated. The results indicate the order of stabilities of the rare earth lactate complexes as: $Lu^{3+} > Yb^{3+} > Tm^{3+} > Er^{3+} > Ho^{3+} > Dy^{3+} > Gd^{3+} > Sm^{3+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > La^{3+}$

The lactate complexes of some rare earths and actinide elements have been studied in solid[1] as well as in solution[2,3]. We have presently determined the stability constants of the lactate complexes of lanthanides(III) pH-metrically in aqueous medium.

All the chemicals used were of AR grade. The rare earth metals were estimated gravimetrically as reported earlier[4]. Ionic strength of 0.1 M was maintained by adding suitable amount of KNO_3 solution. The following two sets of solutions (total volume 50 ml), hereafter referred to as experiment-1 and experiment-2 containing 5.0×10^{-3} g mol of potassium nitrate and the following constituents were titrated pH-metrically against 0.1 N NaOH at $30° \pm 0.5°$C under N_2 atmosphere:

Exp. (1): (a) 3.125×10^{-4} g mol of lacetic acid; and (b) 3.125×10^{-4} g mol of lactic acid and 2.5×10^{-4} g mol of lanthamide nitrate.

Exp. (2): (a) 6.25×10^{-4} g mol of lactic acid; and (b) 6.25×10^{-4} g mol of lactic acid and 2.5×10^{-4} g mol of lanthanide nitrate.

The formation of 1:1 metal complexes in experiment (1) may be represented by Eq. (1)

$$M^{3+} + HL \rightleftharpoons C + nH^+ \qquad \ldots (1)$$

where HL and C represent lactic acid and lactate complex respectively. The charge of the complex, if any, is not shown. The equilibrium constant (K) of the reaction(1) may be expressed by Eq. (2)

$$K = [C][H^+]^n[M^{3+}][HL] \qquad \ldots (2)$$

As derived in the case of cadmium citrate complex[5], it can be shown that

$$\frac{\Delta(NaOH) - a/b\Delta[TL]}{[C]} = n - a/b \qquad \ldots (3)$$

where, $a = k/[H^+]$ and $b = 1 + (k/[H^+])$, $k(1.82 \times 10^{-4})$ being the dissociation constant[6] of lactic acid.

The values of n have been calculated as usual at different pH values and are found to be greater than 1 at pH 4.2, 4.0, 4.0, 3.8, 3.8, 3.8, 3.8, 3.8, 3.6, 3.6, 3.6 and 3.6 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, and Lu lactate systems respectively. The equilibrium constants (K) for the formation of C^{2+} complexes are calculated below these pH values using Eq. (2) and assuming $n = 1$. The mean values of $\log K$ or $-\log K$ thus calculated with standard deviations are: 0.88 ± 0.09 ($-\log K$), 0.58 ± 0.08 ($-\log K$), 0.41 ± 0.09 ($-\log K$), 0.19 ± 0.22 ($\log K$) 0.29 ± 0.15 ($\log K$), 0.35 ± 0.16 ($\log K$), 0.36 ± 0.16 ($\log K$), 0.38 ± 0.16 ($\log K$), 0.41 ± 0.18 ($\log K$), 0.44 ± 0.19 ($\log K$), 0.46 ± 0.19 ($\log K$), 0.48 ± 0.19 ($\log K$), for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu lactate systems respectively. At and above these pH values, n values are >1 and <2 respectively for these systems. Hence above these pH values the complex C^{2+} dissociates according to Eq. (4)

$$C^{2+} \rightleftharpoons C^+ + H^+ \qquad \ldots (4)$$

It can be shown as before[5] that,

$$K_1 = \frac{(n-1)[H^+]}{(2-n)} \qquad \ldots (5)$$

K_1 values have been calculated according to Eq. (5). The mean values of $-\log K_1$ with standard deviations are 5.36 ± 0.17, 5.30 ± 0.24, 5.29 ± 0.2, 4.79 ± 0.08, 4.74 ± 0.03, 4.71 ± 0.03, 4.70 ± 0.02, 4.69 ± 0.02, 4.60 ± 0.05, 4.55 ± 0.08, 4.52 ± 0.11 and 4.47 ± 0.14 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, and Lu lactate systems respectively.

In the 1:2 system (metal-ligand) (Exp. 2), the formation of 1:2 complexes can be represented by Eq. (6) and the equilibrium constant (K) for the reaction (6) may be represented by Eq. (7).

$$M^{3+} + 2HL \rightleftharpoons C_{1:2} + nH^+ \qquad \ldots (6)$$

$$K = \frac{[C_{1:2}][H^+]^n}{[M^{3+}][HL]^2} \qquad \ldots (7)$$

It can be shown that,

$$\frac{\Delta[NaOH] - a/b\Delta[TL]}{[C_{1:2}]} = n - 2 \cdot a/b \qquad \ldots (8)$$

NOTES

The values of n calculated as before at different pH values, are less than 2 below pH 3.8, 4.2, 4.2, 3.8, 3.8, 3.6, 3.6, 3.6, 3.5, 3.5, 3.5 and 3.5 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu lactate systems respectively. The equilibrium constants (K) for the formation of $C_{1:2}^+$ complexes have been calculated below these pH values using Eq. (7), assuming $n = 2$. The mean values of $-\log K$ with standard deviations are 1.71 ± 0.25, 1.65 ± 0.25, 0.86 ± 0.15, 0.80 ± 0.2, 0.74 ± 0.15, 0.72 ± 0.14, 0.69 ± 0.13, 0.68 ± 0.12, 0.66 ± 0.11, 0.64 ± 0.11, 0.62 ± 0.11 and 0.60 ± 0.11 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu systems, respectively.

The values of n are between 2 and 3 in the pH ranges 4.2-5.6, 4.2-5.2, 3.8-5.2, 3.8-4.6, 3.7-4.6, 3.7-4.6, 3.7-4.6, 3.7-4.6, 3.6-4.4, 3.6-4.4, 3.6-4.4 and 3.6-4.4 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu lactate systems respectively. Hence in these pH ranges the complex $C_{1:2}^+$ dissociates to a neutral complex $C_{1:2}$ and a proton according to Eq. (9).

$$C_{1:2}^+ \rightleftharpoons C_{1:2} + H^+ \qquad \ldots (9)$$

It can be shown by proceeding as before that

$$K_1 = \frac{(n-2)[H^+]}{(3-n)} \qquad \ldots (10)$$

K_1 values for all these metal ions have been calculated and the mean values of $-\log K_1$ with standard deviations are 4.8 ± 0.11, 4.55 ± 0.09, 4.22 ± 0.08, 4.14 ± 0.11, 4.13 ± 0.11, 4.12 ± 0.1, 4.11 ± 0.1, 4.09 ± 0.08, 3.87 ± 0.11, 3.86 ± 0.11, 3.85 ± 0.11 and 3.84 ± 0.11 for La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu lactate systems respectively.

References

1 Holm L W & Choppin G R, *J inorg nucl Chem*, 19 (1961) 251.
2 Choppin G R & Chopoorian J A, *J inorg nucl Chem*, 22 (1961) 97.
3 Lesovaya L P & Skrik N A, *Zh neorg Khim*, 18 (1973) 1134.
4 Mohanty N K & Patnaik R K, *J Indian chem Soc*, 54 (1977) 867.
5 Patnaik R K & Pani S, *J Indian chem Soc*, 34 (1957) 673.
6 Cannan R K & Kibrick A, *J Am chem Soc*, 60 (1938) 2314.