Asian Journal of Chemsitry Vol. 8, No. 3 (1996), 425–430

pH-Metric Study on Tervalent Yttrium and Lanthanide Chelates Involving 2-Hydroxy-2-Methyl Propanoic Acid as Secondary Ligand

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Studies on the formation constants for the complexes of the type ML and MAL (where M = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), Lu(III) and Y(III), A = disodium salt of ethylenediamine-tetraacetic acid and HL = 2-hydroxy-2-methyl propanoic acid) have been made at 25°C and 0.1 M ionic strength ($NaClO_4$) by applying Irving-Rossotti pH titration technique and its extension to ternary systems. The order of stability of the MAL complexes was found to be La(III) < Ce(II) < Pr(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III) = Yb(III) < Lu(III).

INTRODUCTION

Potentiometric study on the binary complexes between lanthanide ions and 2-hydroxy-2-methyl propanoic acid[1–5] and chromatographic separation of lanthanide ions by 2-hydroxy-2-methyl propanoic acid as an eluting agent have been reported earlier[6–8]. Moeller and coworkers[9] reviewed the coordination chemistry of yttrium and rare earth metal ions. The present communication describes the determination of the formation constants of yttrium and rare earth metal ions involving 2-hydroxy-2-methyl propanoic acid as secondary ligand(L) and ethylenediaminetetraacetic acid as primary ligand (A) at 25 ± 1°C and 0.1 M ionic strength ($NaClO_4$) by pH titration method.

EXPERIMENTAL

All chemicals used were of A.R. grade. The disodium salt of ethylenediamine tetraacetic acid was used as primary ligand. Carbonate free sodium hydroxide solution was used in pH-metric titrations. The carbonate content of sodium hydroxide was assessed by Gran's method[10]. pH-metric titrations were performed in nitrogen atmosphere at 25 ± 1°C, 0.1 M ionic strength ($NaClO_4$) using a pH-metric model, ECIL-5652 (accuracy ±0.01 pH unit).

In the first experiment, the following two solutions were prepared as per the method followed earlier[11–13]:

1. 0.00625 M HL
2. 0.00625 M HL + 0.005 M Sm(III)

In the second experiment, the following three solutions were prepared as per Irving-Rossotti technique[14]

1. 0.05 M $HClO_4$;
2. 0.005 M $HClO_4$ + 0.005 M HL
3. 0.05 M $HClO_4$ + 0.005 M HL + 0.005 M $Sm(NO_3)_3$

In the third experiment, the following four solutions were prepared as per the method followed earlier[15–17]

(A) 0.05 M $HClO_4$
(B) 0.05 M $HClO_4$ + 0.005 M HL
(C) 0.05 M $HClO_4$ + 0.005 M $Sm(NO_3)_3$ + 0.005 M EDTA
(D) 0.05 M $HClO_4$ + 0.005 M $Sm(NO_3)_3$ + 0.005 M EDTA + 0.005 M HL.

The initial volume in each case was kept 50 mL by the addition of suitable volume of distilled water and the ionic strength was maintained at 0.01 M by the addition of suitable amount of neutral $NaClO_4$ solution. These solutions were pH-metrically titrated by carbonate-free sodium hydroxide solution. Each titration was repeated to get reproducible result.

RESULTS AND DISCUSSION

In the first set of experiments, the number of protons liberated remained 1 and 2 when the metal-ligand ratio was maintained at 1 : 1.25 and 1 : 5 respectively. This indicated the formation of 1 : 1 and 1 : 2 type of complexes.

The reaction taking place between the yttrium and lanthanide ions and 2-hydroxy-2-methyl propanoic acid can be shown as

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

$$M^{3+} + 2HL \rightleftarrows C_{1:2} + nH^+$$

where C represents the complex and n, the number of protons liberated per gram atom of the metal ion. The charge on the complex C depends on the value of n. The value of n was calculated by the method as followed in the cadmium citrate complex[11], tartrate complex[12] of Y(III) and glycolate complex of lanthanide ions[13].

The value of n did not exceed 1.0 in the pH range 2–6 in all the systems studied. Assuming the value of n to be 1 below pH 6, the values of C and then the values of equilibrium constant $-\log K_1^*$ for the reaction (1) were determined as before and the mean values were recorded in Table-1.

During the pH-titrations, insoluble compounds were obtained at pH 7.65 for La(III), 7.42 for Ce(III), 7.39 for Pr(III), 6.81 for Nd(III), 7.30 for Sm(III), 7.17 for Eu(III), 6.71 for Gd(III), 6.93 for Tb(III), 6.99 for Dy(III), 6.65 for Ho(III), 6.85 for Er(III), 6.88 for Yb(III), 7.02 for Lu(III) and 7.09 for Y(III) systems. These insoluble compounds on analysis were found to be the hydroxides of yttrium and lanthanide ions.

In the second set of experiments, the values of $\bar{n}_A$, $\bar{n}$ and pL were calculated by the standard expressions[14]. The formation curves were obtained by plotting $\bar{n}_A$ and $\bar{n}$ against pH and pL respectively. The values of dissociation constant (K_1^H) of 2-hydroxy-2-methyl propanoic acid obtained from the formation curve, $\bar{n}_A$ *vs.* pH, by pointwise calculation and linear plot method were found to agree well with the K_1^H value reported earlier[3]. The most representative value of K_1^H was recorded in Table-1.

TABLE-1
STABILITY CONSTANTS FOR M-L AND M–A–L COMPLEXES AT 25 ± 1°C AND 0.1 M IONIC STRENGTH (N_aClO_4) HL = 2-HYDROXY-2-METHYL PROPANOIC ACID ($pK_1^H = 3.76$)

Metal ion	$-\log K_1^*$	$\log K_1 = \log K_1^*/K_1^H$	$\log K_1$	$\log K^{M-EDTA}_{M-EDTA-L}$
	Experiment-1		Experiment-2	Experiment-3
Y(III)	2.70 ± 0.08	3.06 ± 0.08	2.71 ± 0.07	2.86 ± 0.08
La(III)	3.29 ± 0.01	2.47 ± 0.06	2.47 ± 0.07	2.67 ± 0.09
Ce(III)	3.17 ± 0.08	2.59 ± 0.08	2.64 ± 0.09	2.74 ± 0.08
Pr(III)	3.11 ± 0.07	2.65 ± 0.07	2.67 ± 0.04	2.79 ± 0.08
Nd(III)	2.97 ± 0.09	2.79 ± 0.09	2.79 ± 0.09	2.82 ± 0.08
Sm(III)	2.90 ± 0.09	2.86 ± 0.09	2.87 ± 0.08	2.88 ± 0.09
Eu(III)	2.91 ± 0.08	2.87 ± 0.08	2.92 ± 0.08	2.91 ± 0.10
Gd(III)	2.83 ± 0.08	2.93 ± 0.08	2.98 ± 0.09	2.90 ± 0.09
Tb(III)	2.81 ± 0.06	2.95 ± 0.06	3.05 ± 0.09	2.92 ± 0.10
Dy(III)	2.78 ± 0.10	2.94 ± 0.08	2.95 ± 0.06	2.94 ± 0.09
Ho(III)	2.72 ± 0.08	3.04 ± 0.08	3.05 ± 0.09	2.95 ± 0.07
Er(III)	2.57 ± 0.06	3.19 ± 0.06	3.20 ± 0.08	2.97 ± 0.09
Yb(III)	2.49 ± 0.07	3.27 ± 0.07	3.27 ± 0.09	2.97 ± 0.09
Lu(III)	2.05 ± 0.08	3.71 ± 0.08	3.71 ± 0.10	3.05 ± 0.07

The value of $\bar{n}$ remained between 0.1 and 2.5 in the $\bar{n}$ scale. This indicated the formation of 1:1, 1:2 and 1:3 type of complexes. The $\log K_1$ values were obtained from the formation curve $\bar{n}$ *vs.* pL by half integral method of $\bar{n} = 0.5$. The $\log K_1$ values were also obtained by pointwise and linear plot method. The most representative values of $\log K_1$ were recorded in Table-1. These values of $\log K_1$ agreed well with the respective $\log K_1$ values obtained earlier[1,2]. Only the values of $\log K_1$ were reported here with a view to comparing these values with the respective $\log K^{Ln-EDTA}_{Ln-EDTA-L}$ values of the mixed complexes. It can be shown that the equilibrium constant K_1^* is related to the stability constant K_1 in the following way

$$\log K_1^*/K_1^H = \log K_1$$

The $\log K_1$ values thus obtained in Experiment-1 agreed well with the respective $\log K_1$ values obtained in Experiment-2.

Ln-EDTA-2-Hydroxy-2-methyl propanoic acid systems

In the third set of experiments, the metal : EDTA : 2-Hydroxy-2-methyl propanoic acid ratio was maintained at 1 : 1 : 1. The pH-titration curves for the Sm-EDTA-2-hydroxy-2-methyl propanoic acid system were shown in Fig. 1. The pH-titration curves for Y(III) and other memebrs of the lanthanide series were of similar nature.

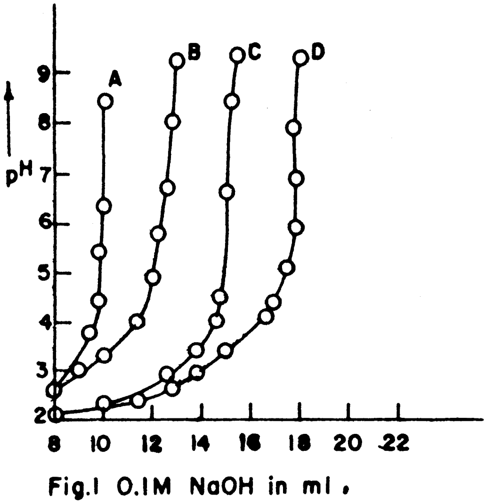

Fig. 1. pH titration of 50 mL solution containing:

Curve A : 0.05 M $HClO_4$ + 0.1 M $NaClO_4$

Curve B: A + 0.005 M 2-hydroxy-2-methyl propanoic acid

Curve C: 0.05 M $HClO_4$ + 0.01 M $NaClO_4$ + 0.005 M $Sm(NO_3)_3$ + 0.005 M Na_2H_2 EDTA

Curve D: C + 0.005 M 2-hydroxy-2-methyl propanoic acid

For the formation of ternary complexes, the necessary conditions like the formation of primary ligand complex, M–EDTA, at low pH and its stability at higher pH at which the combination of the secondary ligand with M–EDTA takes place were satisfied by choosing the secondary ligand (L) in such a way that the stability of the M-L complex was less than that of the primary complex, M–EDTA. Thus the possibility of ligand displacement of the following type was excluded:

$$MA + L \rightleftarrows ML + A$$

The formation of the mixed complex in the present system was therefore assumed to take place in two distinctly separate steps.

$$M + A \rightleftarrows MA$$

$$M + L \rightleftarrows M\text{–}A\text{–}L \quad \text{and} \quad K^{M\text{-}EDTA}_{M\text{-}EDTA\text{-}L} = \frac{[MAL]}{[MA][L]}$$

(Charges were omitted for clarity)

The species present in solution were therefore MA and MAL. The possibility of formation of the MA_2 and ML_2 through reprotonation was excluded.

There may also occur hydrolysis of the primary complex, and even of M(III). In the presence of a bidentate ligand, the complex M–EDTA–L is assumed to be formed in preference of M–EDTA$(OH)_n$. In dilute solution, it was also assumed that the polynuclear species did not exist.

The values of $\bar{n}_{mix}$, the average number of secondary ligands attached to the primary complexes, M–EDTA and pL_{mix}, in the mixed ligand systems, were calculated by an extension of Irving-Rossotti technique[15–17] The plots of $\bar{n}_{mix}/L_{mix}$ *vs.* L_{mix} in the above M–EDTA–L systems were found to be smooth curves (figure not shown). This also suggests the absence of polynuclear and protonated species[17]. The values of $\bar{n}_{mix}$ did not exceed 1 in the $\bar{n}_{mix}$ scale. Therefore, the formation constants, log $K^{M-EDTA}_{M-EDTA-L}$ were evaluated by the method of interpolation at various $\bar{n}_{mix}$ values. The values of formation constants thus obtained were recorded in Table-1.

The values of the stability constants, log K_1 of the Ln–L complexes for the light rare earths (*i.e.*, from La–Eu) were found to be less than those of the corresponding stability constants of the Ln–A–L ternary complexes while the stability values of the Ln–L complexes for the heavy rare earths (*i.e.*, Tb–Lu) were found to be more than those of the corresponding Ln–A–L complexes. This may be due to the fact that in the light rare earth region (*i.e.*, La–Eu) the inductive effect of the methyl group in 2-hydroxy-2-methyl propanoic acid contributes significantly for the stability of the Ln–A–L complexes.

The ionic radii of lanthanide ions regularly decrease with increase in atomic number. In the heavy rare earth region the lowering in the stability value of the Ln–A–L complex with respect to the stability values of the Ln–L complex can be ascribed to the inability of the 2-hydroxy-2-methyl propanoic acid to adapt to the smaller lanthanide ions. The position of yttrium with respect to the magnitude of the formation constant of its Y–L complex in the present study is found between holmium and erbium and for the Y–A–L ternary complex its position is found between neodymium and samarium. Such erratic behaviour of Y(III) has been reported elsewhere[9].

ACKNOWLEDGEMENTS

The authors are thankful to Prof. K.K. Tripathy, Head of the Department of Chemistry and Prof. S. Misra, Principal, Regional Engineering College, Rourkela for extending necessary research facilities.

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(*Received*: 5 October 1995; *Accepted*: 18 January 1996) AJC-1067