

Formation of Binary & Ternary Chelates of Calmagite with Lanthanides in Presence of Some Amino Polycarboxylic Acids

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The formation constants of 1:1 and 1:2 binary Ln(III)-calmagite (CLM) and 1:1:1 ternary [Ln(III)-CLM-A] chelates [where Ln(III)=La, Pr, Nd, Gd, Dy and Y; A=iminodiacetic acid (IMDA), hydroxyethyliminodiacetic acid (HIMDA) and nitrilotriacetic acid (NTA)] have been determined *pH*-metrically in 50% (v/v) aq. methanol medium at 30°C and *I*=0.1 *M* (NaClO₄). The ligand calmagite coordinates as a secondary ligand in presence of IMDA, HIMDA and NTA with all the metal ions. The order of formation constants of binary as well as ternary chelates is found to be: La < Pr < Nd < Gd < Dy > Y.

Calmagite [1-(2-hydroxy-5-methylphenylazo)-2-naphthol-4-sulphonic acid] (CLM) has been widely used as a metallo-chromic indicator in the complexometric titrations^{1,2}. Calmagite offers an advantage in that its aqueous solution is more stable than that of Eriochrome Black-T. Recently, studies have been made on the ternary complex formation of Eriochrome Black-T chelates with lanthanides in presence of HIMDA, NTA, EDTA and CDTA³. A survey of literature reveals that little work has been done with the ligand calmagite. Therefore, it was thought worthwhile to investigate the complexation reactions of calmagite with Ln(III) ions in the presence of aminopolycarboxylic acids.

We report here the potentiometric determination of formation constants of 1:1 and 1:2 binary chelates of calmagite with La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III) ions and formation of mixed ligand complexes of lanthanides with calmagite and aminopolycarboxylic acids, viz., iminodiacetic acid (IMDA), hydroxyethyliminodiacetic acid (HIMDA), nitrilotriacetic acid (NTA), cyclohexanediaminetetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyl ethylenediaminetriacetic acid (HEDTA) and ethylenediaminetetraacetic acid (EDTA) in 50% (v/v) aq. methanol at 30°C and *I*=0.1 *M* (NaClO₄).

Calmagite was purified by the method of Lindstrom *et al.*⁴. The other reagents NaClO₄ (E Merck), EDTA (BDH), NTA (Sigma), CDTA (E Merck), DTPA (BDH), IMDA (Sigma), HIMDA (Fluka), HEDTA (Fluka) of AR/GR grade were used without further purification. Proton-ligand formation constants of calmagite and the metal-ligand formation constants of its lanthanide chelates were determined *pH*-metrically by Irving-Rossotti titration technique⁵. The formation constants of ternary systems were determined by the method of Ramamoorthy and Santappa⁶. *pH* meter readings (B) in 50% (v/v) methanol-water were corrected by the method of Van Uitert and Haas⁷.

The *pK* values of calmagite, determined *pH*-metrically, were found to be 8.20 and 11.83. They correspond to the dissociation of hydroxyl groups in the molecule. The -SO₃H group present in the molecule dissociates at much lower *pH* (*pH* < 2.0) and therefore its dissociation constant could not be determined. The values obtained in the present study are in good agreement with the values (8.14 and 12.35) reported earlier by Lindstrom and Diehl¹, which were determined spectrophotometrically in aqueous medium at 25°C.

The \bar{n} (degree of formation) values (0.1 < \bar{n} < 1.9) obtained for Ln(III)-CLM system indicate the formation of 1:1 and 1:2 complexes. The ligand CLM starts coordinating with lanthanide ions at *pH* 5.5, 4.8, 4.7, 4.0, 4.0 and 4.2 for La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III) respectively. Formation of 1:2 chelates with Ln(III) ions may be explained in the light of their large size and high positive charge coupled with their tendency to attain higher coordination numbers.

In the ternary system the ratio of concentration of Ln(III), calmagite and aminopolycarboxylic acid (A) was maintained at 1:1:1, the concentration of each being kept at 0.001 *M*. In the ternary systems studied, the mixed ligand curves closely follow the 1:1 Ln(III)-A (where A=IMDA, HIMDA and NTA) binary curves in the lower *pH* (< 4.0) region, until the protons of aminopolycarboxylic acid are neutralized, indicating that the binary Ln(III)-A complexes predominate in this region. Above this region the divergence of the ternary curve from those of the binary Ln(III)-A systems reveals the formation of ternary complexes of the type [Ln-A-CLM]. Here, calmagite acts as a

Table 1 – Equilibrium Constants of Binary and Ternary Metal Chelates of Some Lanthanides with Calmagite (L) and Iminodiacetic Acid, Hydroxyethyliminodiacetic Acid, Nitritotriacetic Acid in 50% (v/v) Aq. Methanol

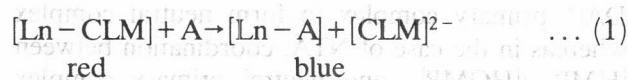
[I = 0.1 M (NaClO₄); temp. = 30°C]

Constant*	La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)	Y(III)
$\log K_{ML}^M$	10.78	12.13	12.38	13.18	13.48	13.08
$\log K_{ML_2}^{ML}$	7.44	8.97	9.42	9.87	10.09	9.70
$\log K_{MAL}^{MA}$						
	A = IMDA					
	9.35	10.34	10.65	11.32	11.58	11.34
	A = HIMDA					
	8.68	9.57	9.88	10.57	10.79	10.59
	A = NTA					
	8.20	8.81	9.01	9.89	10.27	9.82
$\Delta \log K$						
	A = IMDA					
	-1.43	-1.79	-1.73	-1.86	-1.90	-1.74
	A = HIMDA					
	-2.10	-2.56	-2.50	-2.61	-2.69	-2.49
	A = NTA					
	-2.58	-3.32	-3.37	-3.29	-3.21	-3.26

*Standard deviations are within $\pm 0.05 \log K$ units.

secondary ligand. The formation of ternary complexes is further supported by (i) intensification of colour and (ii) non-superimposable nature of the theoretical composite curve in the region of mixed-ligand complex formation⁸.

However, in the case of HEDTA, EDTA, CDTA and DTPA the superimposable nature of theoretical composite curve with the experimental titration curves indicates that calmagite does not coordinate with the primary [Ln-A] complex. This may be due to the hexadentate nature of CDTA, EDTA and HEDTA or octadentate nature of DTPA. This is further supported by the formation of blue colour (due to free CLM ion) in the pH range above 7.0 when Ln(III) ions are titrated with CDTA, EDTA, HEDTA or DTPA in presence of CLM. Hence these titrants replace [CLM]²⁻ from [Ln-CLM] complexes at pH > 7.0,



where A = EDTA, HEDTA or DTPA.

The relative order of stabilities in all the metal-ligand systems [La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) > Y(III)] is almost in accordance with increasing charge/radius ratio of the metal ions. The linear plots between $\log K_1$ and Z^2/r (r is the radius of the metal ion) for various Ln(III) ions show that metal-CLM bond is primarily ionic in character⁹.

The extent of favoured formation of the ternary complexes can be inferred from $\Delta \log K$ values¹⁰. The negative $\Delta \log K$ values (Table 1) reveal that the formation of ternary complexes is not favoured over that of binary complexes. This may be due to the availability of lesser number of co-ordinating sites for calmagite on primary complex [Ln-A] than on the free Ln(aq)³⁺ ions¹¹.

The order of stabilities with respect to primary ligands is IMDA > HIMDA > NTA. This is due to the charge neutralization in the formation of the mixed chelates¹⁰ as well as denticity of the ligands. In the case of IMDA and HIMDA, coordination of [CLM]⁻ occurs with mono positive [Ln-IMDA]⁺ or [Ln-HIMDA]⁺ primary complex whereas in the case of NTA, it is between [CLM]⁻ and a neutral primary complex [Ln-NTA]. Therefore, more electrostatic attraction is expected between [CLM]⁻ and [Ln-IMDA/HIMDA]⁺ than that between [CLM]⁻ and [Ln-NTA] complex. A perusal of $\Delta \log K$ values also confirms the above trend.

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