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ABSTRACT

A quantitative study of the interaction of some lanthanide ions with 1,2-diamine cyclohexane N,N'-tetraacetic acid (DCTA) was carried out. Stability constants of the formed lanthanide chelates were calculated. A discussion of the variation of the metal chelates stability constants across the lanthanide series was given.

INTRODUCTION

On the basis of many well established instances of ionic bonding in lanthanide complexes, it has been quite generally concluded that the stabilities of trivalent lanthanide complexes, specially with polyaminopolycarboxylic acids, should increase with decreasing cation radius or increasing atomic number (1). There appears to be no uniform increase in the stability with increasing atomic number. There is a "break" at gadolinium. The stability of the lanthanide complexes with ethylenediaminetetraacetic acid (EDTA) has one constant value from terbium through lutetium (2). Similar observations were found in case of lanthanide chelates with N-hydroxyethylenediaminetriacetic acid (3), propylenediaminetetraacetic acid (4), 1,2-bis [2-di (carboxy methyl) aminoethoxy] ethane (5) and diethylenetriaminepentaacetic acid (6). The ga-

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dolinium break for chelates with ethylenediaminetetraacetic acid has been ascribed to a change in the number of co-ordinating positions occupied by the ligand (7). The present work is an extention of this approach to 1,2-diamine cyclohexane N,N'-tetraacetic acid (DCTA).

EXPERIMENTAL

All chemicals were of analytical grade reagent. Lanthanide metal oxides were of 99.99% purity. DCTA was recrystallised twice from ether. Solutions of lanthanide metal chloride were obtained by disolving an accurate weighed quantities of the oxides in 1N HCl and were titrated complexometrically using Eriochrome black T (7). The chelate solution, of each element was prepared by mixing, at acidic medium, a known volume of 8×10^{-2} M. lanthanide ion with the same volume of known concentration of DCTA. The pH was then adjusted using sodium hydroxide free carbonate. All pH measurements were made using Unicum pH meter of type 292. The optical measurements were done by Prolabo spectrophotometer.

The stability constant (pK) of each complex was calculated using Job's equation (8). The dissociation constants of DCTA were taken equal to 2.4, 3.5, 6.12 and 11.7 respectively (9).

RESULTS AND DISCUSSION

1– Variation of the absorption spectrum of a mixture of (Ln^{+3} + DCTA) as a function of pH:

The absorption spectra of 4×10^{-2} M of Pr III, Nd III, Sm III, Eu III, Gd III, Dy III or Er III, in 1N HCl have characteristic maxima in the region of wavelengthes lying between $\lambda = 250$ nm and $\lambda = 600$ nm (Fig. 1). The DCTA absorbs in the U.V. region, its absorbance is negligable from $\lambda \lesssim 280$ nm. Absorption spectra of a mixture of either 4×10^{-2} M Pr III, Nd III, Sm III, Eu III, Gd III, Dy III or Er III and 1.6×10^{-1} M DCTA were measured as a function of pH. The spectra of the lanthanide ions were found to be slightly shifted to longer wavelengthes with an increase in the intensity as the pH of the mixture solution was increased. Within certain pH ranges, the position of the absorption maxima remained constant (Fig. 1). It should be mentioned that the shift of the absorption maxima to the higher wavelength is more clearly observed in case of praseodymium and samarium than in that of dysprosium and erbium. The pH, at which the corresponding complex compound, begins to form is in case of erbium in more acid region than in case of praseodymium. This is apparently because praseodymium has more basic properties and therefore the formation of its complexes takes place in a more basic region. The pH intervals for complete chelation and the characteristic wavelengthes of each complex, are given in Table 1.

TABLE I

Characteristics of lanthanide - DCTA chelates

Ion	λ nm	λ nm complex	pH intervals	pK
Pr III	442 466 478	444 468 482	3.7 - 10	16.3
Nd III	518 571	522 576	3.4 - 10	16.6
Sm III	344 360 400	346 362 403	3.11 - 10	17.2
Eu III	392	394	2.9 - 10	17.6
Gd III	272 275.5	273 276	2.6 - 10	17.6
Dy III	324 349 363	326 352 362	2.3 - 10	17.8
Er III	255 377 483 517.5	256 376 486 518	2.0 - 10	18.0

2- Determination of the composttion of the chelate:

The composition of the chelates was determined at pH 4.5 and 7.5 using a) the mole ratio method (Fig. 2) in which the $[Ln^{+3}]$ was kept constant at 4×10^{-2} M and b) the continuous variation method in which $[Ln^{+3} + DCTA]$ was kept constant at 8×10^{-2} M. Obtained results showed that the formed chelates had the composition of 1/1. It was found that solutions containing 1/1 of Ln^{+3} and DCTA did not give a precipitate up to pH 9.5 while a precipitate was noticed at $[Ln^{+3}]/[DCTA] = 3/2$ and clearly at $[Ln^{+3}]/[DCTA] = 2/1$. This indicates that only 1/1 complex is formed.

The stability constants values were calculated, at pH 4.5, and are given in Table 1. Results show that, a regular increase in stability of the 1/1 chelates with increasing atomic number from Pr^{+3} through Eu^{+3} and a discontinuity at Gd^{+3} is noted. It was suggested by many authors (1, 3, 7) that the bonding in such chelates (with polyaminopolycarboxylic acids) is purely electrostatic and therefore the stability of these complexes (pK) should be determined only by the radius of the cations present and should then be expected to vary linearly with Z^2/r (where Z is the atomic number, r is the radius of the cation). Such linearity characterizes the (Pr III + DCTA) chelates to the (Eu III + DCTA) chelates. For ions beyond Gd^{+3}, normal further increase in stability with decreased radius is occurred. It can be argued that the gadolinium break is related to the discontinuity in crystal radius at gadolinium. Moreover it was suggested, in case of EDTA, that (10), because of the many possible co-ordination sites in the polyaminopolycarboxylic ligands, there is a possibility of a change in the number of points of attachment before and after gadolinium and due to the bulkness of the carboxyl groups, a critical point in crystal radius might be reached beyond which only three of the four carboxyl groups could fit about the central ion. The gadolinium break was thus associated with a change from sexidentate to quinquedentate behaviour on the part of the ligand. Such explaination can be applied in case of (DCTA + lanthanide) complexes. Staveley and Randall (11) have suggested that, the above trend in formation constants may be due to varing degrees of stabilization from the interaction of the 4f orbitals with the ligand field.

Therefore the differencess between the stability constants for the successive (DCTA + lanthanide) complexes which are less for ions byond gadolinium than ions before are due; to the irregular decrease of the crystal radius of lanthanides, to the change in the co-ordination number across the lanthanides and to some extent to the charing of 4f orbital in the bonding of the lanthanide ion to DCTA.

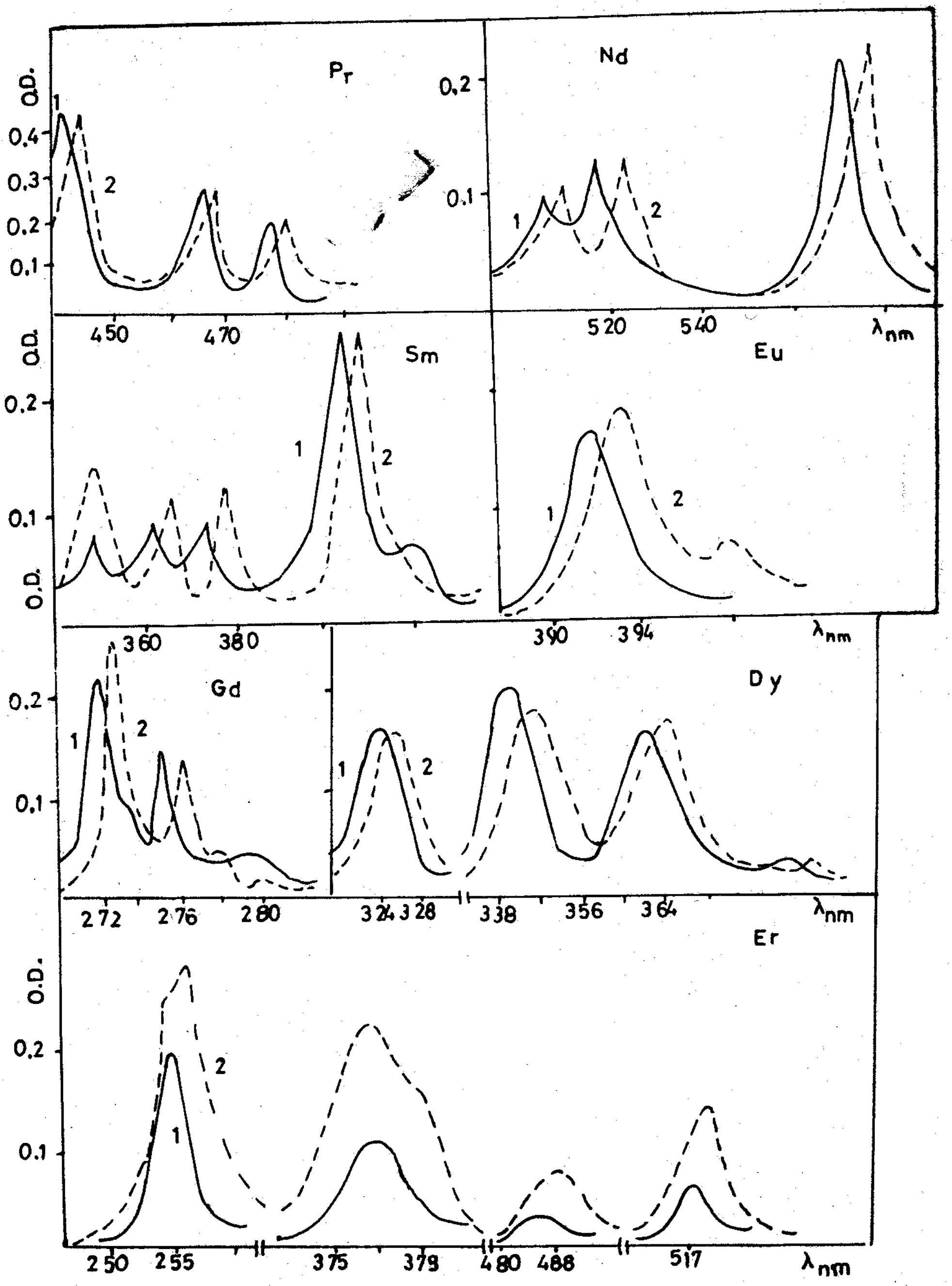

Fig 1. Absorption spectra of: (1) Ln^{+3} only in 1 N HCl, (2) $[Ln^{+3}]$ / [DCTA] = 1/4 at pH 4.5. $[Ln^{+3}] = 4\times10^{-2}$ M.

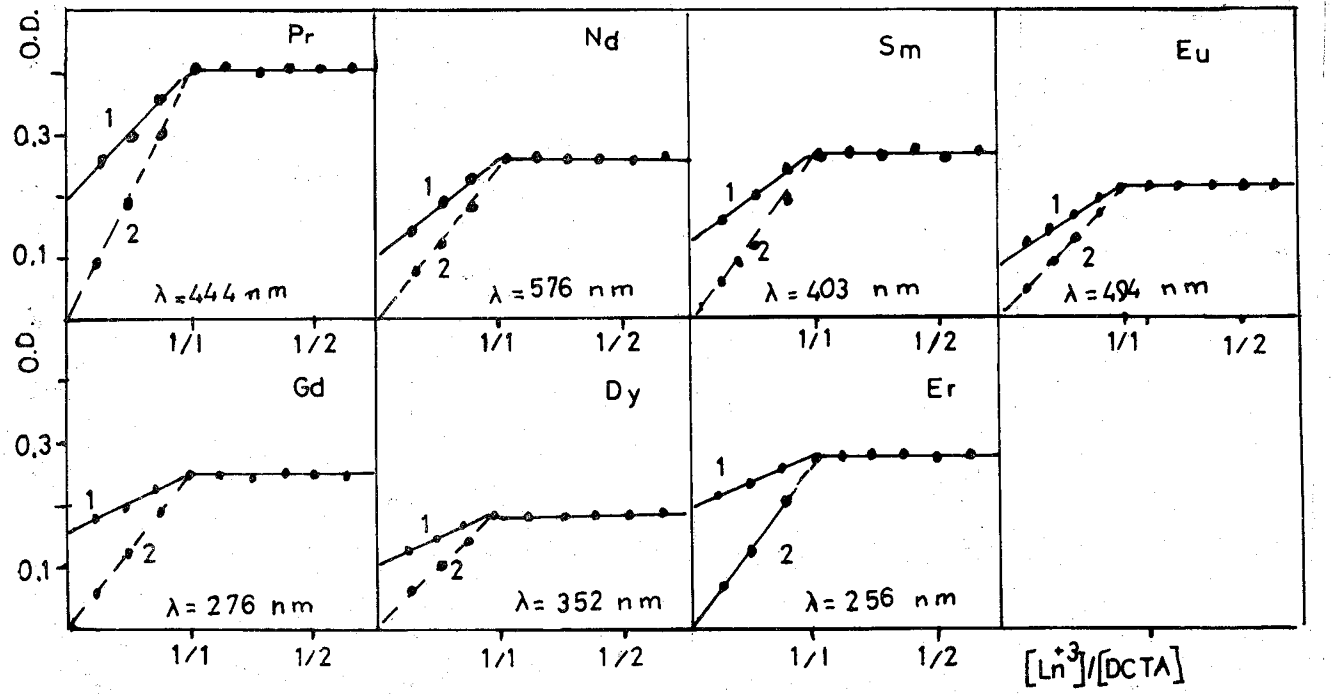

Fig. 2. Variation of the optical density at the characteristic wavelength of each lanthanide complex, as a function of (DCTA) concentration. (1) pH = 4.5 and (2) pH = 7.5. $[Ln^{+3}] = 4 \times 10^{-2}$ M.

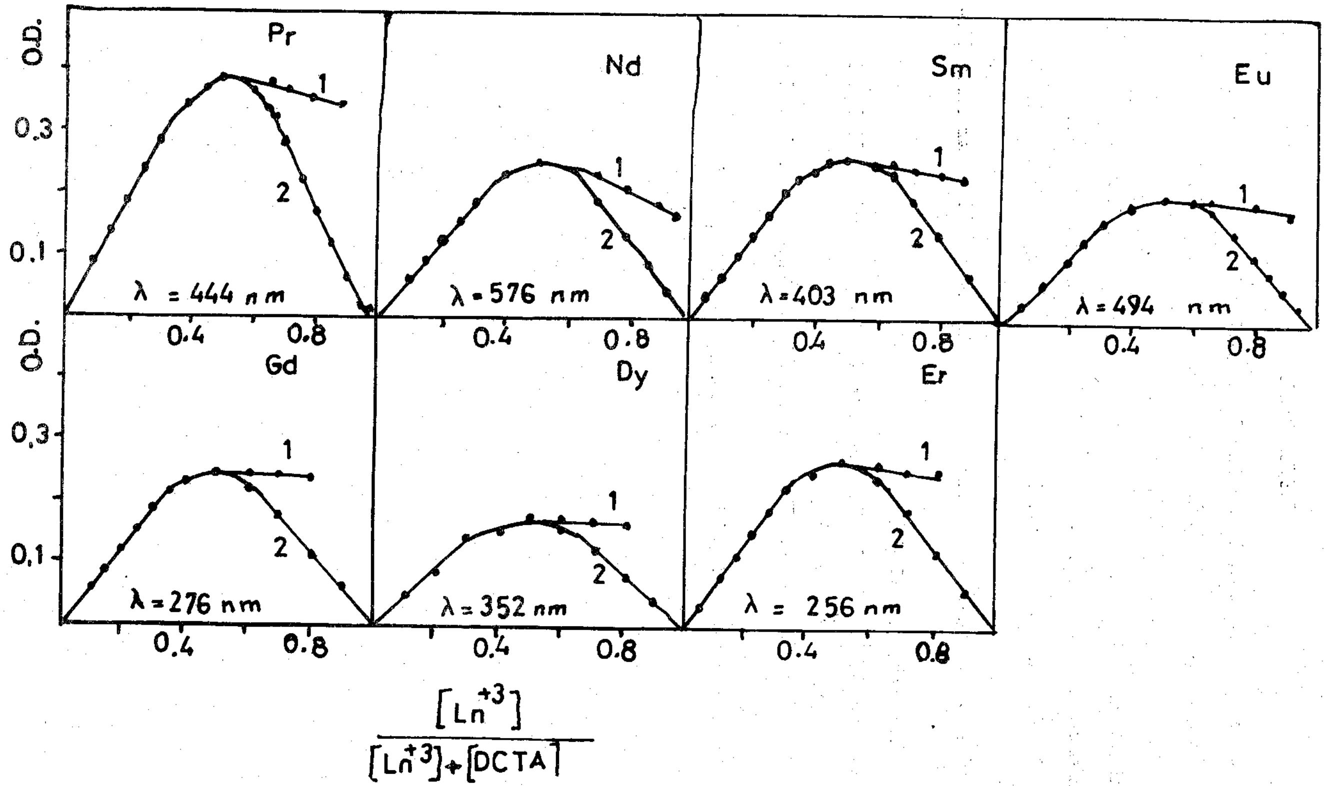

Fig 3. Variation of the optical density at the characteristic wavelength of each lanthanide complex, as a functionof $[Ln^{+3}]$ /([DCTA] + $[Ln^{+3}]$), (1) pH = 4.5 and (2) pH = 7.5. $[Ln^{+3}$ + DCTA] = 8×10^{-2} M.

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