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Mixed Ligand Complexes of Lanthanides with Macrocyclic and Open-chained Polyaminopolycarboxylic Acids and Acetylacetone

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Abstract

Studies of mixed ligand complex formation stabilities and dissociation kinetics have been performed on lanthanide ions with macrocyclic and open-chained polyaminopolycarboxylic acids (*i.e.* DAPDA, DACDA, EDDA, and EDTA) and acetylacetone (acac). From UV spectroscopic evidence, it was found that $Ln(DACDA)^+$ and $Ln(EDTA)^-$ complexes do not form mixed ligand complexes with acac under the set conditions, *i.e.* pH = 7.2 and complex concentration of 1×10^{-4} M. On the other hand, formation of Ln(DAPDA)(acac) and $Ln(EDDA)(acac)_2^-$ complexes were readily detectable. The mixed complex formation constants, β_1, for the equilibrium $Ln(L)^+ + acac^- \rightleftharpoons Ln(L)(acac)$, and β_2, for the equilibrium $Ln(L)^+ + 2\ acac^- \rightleftharpoons Ln(L)(acac)_2^-$ were determined by potentiometric titration technique where possible. It was found that β_1 values were in general greater for $Ln(EDDA)^+$ complexes than for $Ln(DAPDA)^+$ complexes indicating the resulting reduced charge density at the lanthanide ion of $Ln(DAPDA)^+$ and that less space is available for the acetylacetone moiety to coordinate to the $Ln(DAPDA)^+$ complexes due to the large size and the greater number of coordination atoms of DAPDA. The hydrolysis constants of $Ln(EDDA)(H_2O)_n^+$ species were also determined and were found to be increasing with increasing atomic number of Ln. Attempts to measure the acid assisted mixed ligand complex dissociation rates by a stopped-flow spectrophotometer were not fruitful due to the much faster rates.

Introduction

The study of mixed ligand complex formation and dissociation kinetics has been of interest for a number of years [1]. Recently, enhanced stability of ternary Cu(II) or Pd(II) complexes was reported due to either intramolecular hydrophobic [2–4] or electronic [5, 6] ligand–ligand interactions. Stereoselectivity was also observed for diastereomeric chiral ternary complexes [7–10]. On the other hand, the reaction of $Ni(trien)^{2+}$ with ethylenediamine (en) was shown to have a rate-determining ring-closure step as a result of coordination angle distortion in the nickel coordination sphere that was due to coordinated trien, *i.e.* a kinetic steric effect is evident [11]. The fundamental knowledge obtained usually leads to a better understanding of chemical applications of ternary complex systems such as biological enzyme-metal-substrate interactions, distinct protein structural features, ligand exchange chromatography, as well as synergistic solvent extractions of metals.

In an effort to the design, synthesis, and characterization of lanthanide ion selective reagents, we have prepared two macrocyclic compounds with acetic acid ionizable pendant arms, *i.e.* 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21-DA or DAPDA) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (K22-DA or DACDA), (Fig. 1). Both complex formation stabilities and acid-catalyzed dissociation rates of lanthanide complexes of the two ligands have been reported [12, 13]. In particular, it was seen that DAPDA, the macrocyclic ligand with a 15-membered ring forms

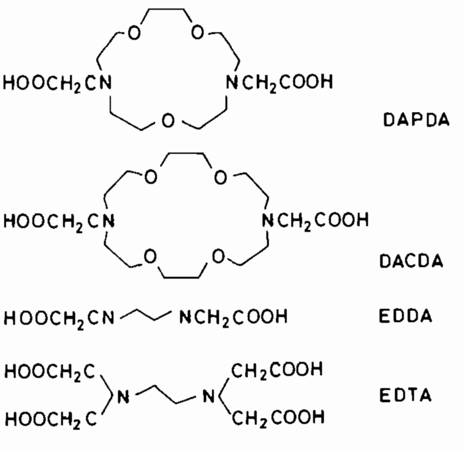

Fig. 1. Structures of DAPDA, DACDA, EDDA, and EDTA.

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strongest complex with Eu(III) among all lanthanides while DACDA, the 18-membered ring structural analogue, forms stronger complexes with the first five lighter lanthanides.

In view of the respective 7- and 8-coordination capability of DAPDA and DACDA as well as the possibility of lanthanide forming higher order mixed ligand complexes for solvent extraction applications, we have carried out studies of mixed ligand complex stability and kinetics using acetylacetone as the auxiliary ligand. For comparison purpose, two open-chained structural analogues, *i.e.*, ethylenediamine-*N,N'*-diacetic acid (EDDA) and ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA), (Fig. 1), are also included under similar or identical experimental conditions. The results are reported in this paper.

Experimental

Materials and Standard Solutions

The ligands, DAPDA and DACDA, were prepared and purified according to the published methods [12]. EDDA, disodium salt of EDTA, and acetylacetone were of reagent grade and purified by recrystallization in 1:1 water/ethanol solution and by vacuum distillation, respectively.

Aqueous stock solutions of ligands (DAPDA, DACDA, EDDA and disodium salt of EDTA) were prepared as $\sim 1 \times 10^{-2}$ M and standardized accordingly. Acetylacetone solution was prepared by diluting an appropriate weighed amount of redistilled sample. Carbonate-free tetramethylammonium hydroxide solution (0.05 M) was prepared by diluting a 20% $(CH_3)_4NOH$ methanol solution from Aldrich Chemical Co. and standardized by using potassium hydrogen phthalate. The standard metal salt solutions having concentrations about 0.01 M were prepared from reagent grade nitrates or chlorides and standardized according to the previously published procedure [12]. A 1 M solution of $(CH_3)_4NCl$ was prepared and determined by passing aliquots of the solution into a cation-exchange (Dowex 50W-X8 resin) column in the H^+ form and by titrating the displaced H^+ ions with standard KOH solution.

Potentiometric Titrations

All titrations were carried out at constant ionic strength of 0.10 M $(CH_3)_4NCl$. Boiled deionized 18Ω water was used for all experiments. A Model 750 Fisher Accumet selective ion analyzer or a Fisher Model 825 MP pH meter in conjunction with a Fisher combination pH electrode was employed to monitor the pH (±0.001 pH unit). The exact procedure for the determination of mixed ligand complex formation constants was similar to the method of Thompson and Loraas [14] and that of Martell *et al.* [15].

Spectrophotometric and Kinetic Measurements

Spectrophotometric measurements were made on a Perkin-Elmer 552 spectrophotometer. Kinetic measurements were performed using a Durrum-Dionex stopped flow spectrophotometer, model D-110, interfaced to a computer work station. TRIS buffer was used to adjust pH if not stated otherwise.

Results and Discussion

Ultraviolet Absorption Spectroscopy

UV absorption spectra of acac as well as its conjugate base show two absorptions each with maxima at 274 nm/203 nm and 293 nm/211 nm, respectively. Absorption corresponding to higher energies are relatively weaker in intensities. Nitrate ion as well as TRIS buffer employed in the present work were found to absorb significantly in the region below 230 nm. Accordingly absorption corresponding to lower energy was used for the present investigations. Wavelength maxima as well as molar absorptivity of this absorption varied with hydrogen ion concentration as predicted. pKa value of acetylacetone as determined using different wavelengths is 8.87 ± 0.03, consistent with the literature value.

Present investigations on the complexation behaviour of acac with cationic complexes of lanthanides $(LnL)^+$ were carried out at pH varying from 7 to 7.3 due to the following reasons:

(a) Potentiometric studies carried out on the formation of cationic complexes of lanthanides (concentration 3×10^{-3} M) with EDDA, DAPDA and DACDA revealed that the complexation is quantitative only at pH > 7.0;

(b) Degree of complexation of acac increases with pH;

(c) Hydrolysis of lanthanides is significantly large at pH > 7.0 ($\log k_h = -8.0$);

(d) Difference in wavelength maxima of uncomplexed acac and complexed acac decreases with increase of pH above pH = 7.0.

Figure 2 shows the UV absorption spectra of various complex systems investigated in the present work employing Yb^{3+} as a typical lanthanide ion in the pH range 7 to 7.3. No change in λ_{max} was observed in the case of DACDA as well as EDTA complexes of Yb^{3+} suggesting that acac does not coordinate with them. It is probably due to the saturation of coordination number in case of DACDA complex and due to electrostatic repulsion of $acac^-$ with the anionic complex of EDTA. On the other hand, changes in UV absorption maxima can be clearly seen (Fig. 2) in DAPDA as well as EDDA systems. Shift in case of DAPDA complex was smaller

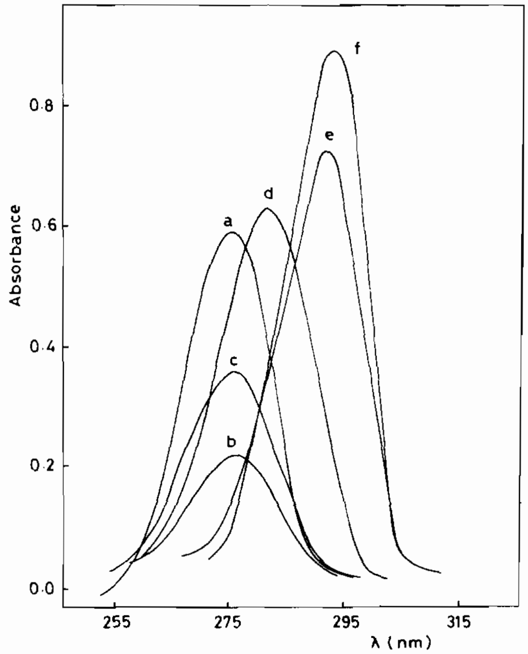

Fig. 2. Absorption spectra of several mixed ligand systems, pH = 7.0 TRIS buffer). (a) 4×10^{-4} acac; (b) 1×10^{-4} M Yb^{3+} + 1×10^{-4} M DACDA + 1.4×10^{-4} M acac; (c) 2×10^{-4} M Yb^{3+} + 2×10^{-4} M EDTA + 2×10^{-4} M acac; (d) 1×10^{-4} M Yb^{3+} + 1×10^{-4} M DAPDA + 4×10^{-4} M acac; (e) 1×10^{-4} M Yb^{3+} + 1×10^{-4} M EDDA + 4×10^{-4} M acac; (f) 1×10^{-4} M Yb^{3+} + 4×10^{-4} M acac.

(~6 nm) as compared to that of EDDA complex (~16 nm), which in turn was found close to the one observed for binary Yb–acac system (~18 nm). The magnitude of shifts is probably related to the degree of complexation in these cases.

Stoichiometry of the mixed ligand complexes formed was followed by employing molar ratio method. Figure 3 shows the variation of absorbance with concentration of acac for Yb–EDDA system at pH = 7.26 for wavelengths 290 nm as well as 310 nm. Slope variation was observed at [acac]/[Yb $EDDA^+$] of approximately 2.0, indicating the stoichiometry of the complex species as $Yb(EDDA)(acac)_2^-$. Similarly, Fig. 4 shows the stoichiometry of the complex species formed in case of Yb^{3+}–DAPDA system as Yb(DAPDA)(acac). Stoichiometry in the EDDA system was further confirmed using Job's method of continuous variation. Studies carried out on the Eu^{3+}–DAPDA–acac and Lu^{3+}–DAPDA–acac system revealed that the nature of absorption spectra does not vary significantly with the metal ion.

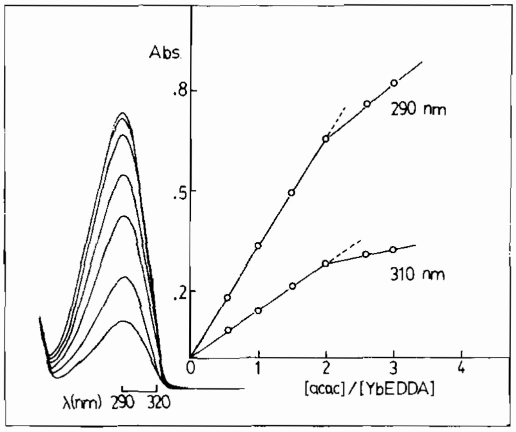

Fig. 3. Molar ratio plots of Yb–EDDA–acac system, [YbEDDA] = 1.0×10^{-4} M, pH = 7.0.

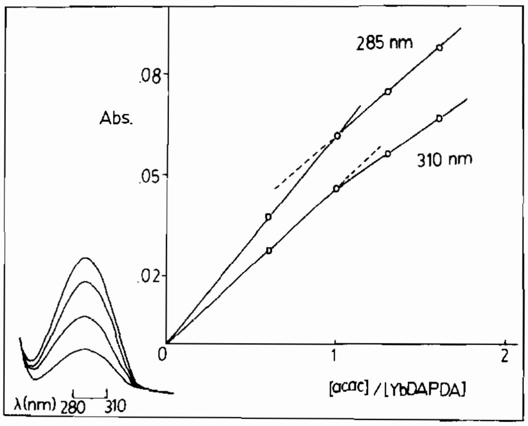

Fig. 4. Molar ratio plots of Yb–DAPDA–acac system, [YbDAPDA] = 1.0×10^{-4} M, pH = 7.1.

The ternary complex formation of Ln–DAPDA and Ln–EDDA with acac may be expected because lanthanide ions often form complexes with eight or nine coordination numbers. Since neither DAPDA (7 donor atoms) nor EDDA (4 donor atoms) can satisfy the coordination requirement, additional acetylacetonate ion(s) complexation is then possible.

Attempts were made using the method of corresponding solutions [16, 17] to determine the formation constants of the ternary complex, $Yb(EDDA)(acac)_2^-$, at pH = 7:

$$Yb(EDDA)^+ + acac^- \overset{\beta_1}{\rightleftharpoons} Yb(EDDA)(acac) \qquad (1)$$

$$Yb(EDDA)^+ + 2acac^- \overset{\beta_2}{\rightleftharpoons} Yb(EDDA)(acac)_2^- \qquad (2)$$

It was shown that log β_1 is ~6 and log β_2 could not be accurately determined. This was confirmed by a redetermination of β_1 and β_2 values of Yb–acac complexes. Indeed, the log β_1 value, for the Yb–acac complex, 6.32, is in conformity with the literature value (6.18) and the present log β_2 (5.8) was one order of magnitude higher than the accepted one (4.86). Potentiometric titration method was then employed to determine formation constants.

Potentiometric Titrations

The potentiometric titration of Ln–DAPDA–acac system was straight forward. A mixture of 1:1:1 solution (1×10^{-3} M) of Ln^{3+}, DAPDA, and acetylacetone was titrated by standard $(CH_3)_4NOH$ solution.

The ternary complex formation occurs in a stepwise fashion as judged from the titration curve:

$$Ln^{3+} + DACDA^{2-} \overset{K_1}{\rightleftharpoons} Ln(DACDA)^{+} \qquad (3)$$

$$Ln(DACDA)^{+} + acac^{-} \overset{K_2}{\rightleftharpoons} Ln(DACDA)(acac) \qquad (4)$$

From the lowered pH buffer zone corresponding to the neutralization of proton attached to acetylacetone, one is able to determine K_2 values as shown in Table I. It is believed that both steric hindrance as well as charge density of the lanthanide ion is important to interpret the data. Thus, the smallest Lu(III) may have relatively little room available for the acetylacetonate ion to coordinate, resulting in low ternary complex formation constant. On the other hand, La(III) may have enough room for acac coordination but the slightly low charge density of complexed La(III) precludes from attaining the highest stability. Among the five lanthanide ions studied, Er(III) turns out to form the strongest ternary complex with acac.

TABLE I. Ternary Complex Formation Constants of Ln-(DAPDA)(acac). System: $Ln(DAPDA)^{+} + acac^{-} \overset{K_2}{\rightleftharpoons}$ Ln-(DAPDA)(acac). Ionic strength = 0.10, 25 °C.

Ln(III)	log K_2
La	3.14 ± 0.11
Eu	3.04 ± 0.18
Er	3.49 ± 0.07
Yb	3.25 ± 0.29
Lu	2.70 ± 0.09

Since Ln–EDDA systems form complexes with two acac molecules, the titration procedure is slightly different. Figure 5 shows typical titration plots for $La(EDDA)(acac)_2^{-}$ system. Curve I and II are the titrations of the ligands acetylacetone (2 equivalent) and EDDA (1 equivalent), respectively. Curve III is the titration of 1:1 mixture of La(III) ion and EDDA which also determines the hydrolysis constants of Ln(EDDA) complexes.

$$Ln(EDDA)(H_2O)_n^{+} \overset{K_h}{\rightleftharpoons} Ln(EDDA)(OH)(H_2O)_{n-1} + H^{+} \qquad (5)$$

The K_h values so obtained are listed in Table II. A trend is observed, *i.e.*, the smaller the size and greater the charge density of the lanthanide ion, the lower the log K_h value.

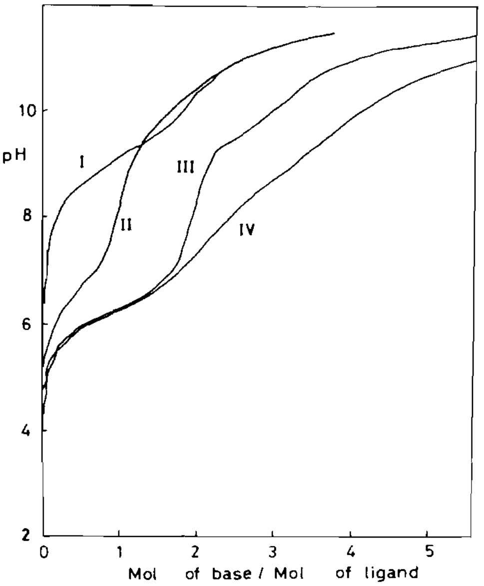

Fig. 5. Typical titration plots to determine mixed ligand complex formation stability constants of Ln–EDDA–acac system. $[Ln] = [La^{3+}] = 1.0 \times 10^{-3}$ M, $[EDDA] = 1.0 \times 10^{-3}$ M, $[acac] = 2.0 \times 10^{-3}$ M. Ionic strength = 0.10 (KNO_3), 25 °C.

TABLE II. Hydrolysis Constants (K_h) of $Ln(EDDA)(H_2O)_n^{+}$ Complexes.

$$Ln(EDDA)(H_2O)_n^{+} \overset{K_h}{\rightleftharpoons} Ln(EDDA)(OH)(H_2O)_{n-1} + H^{+}$$

Ln(III)	–log K_h
La	9.44 ± 0.05
Eu	8.06 ± 0.05
Er	7.72 ± 0.05
Yb	7.39 ± 0.05
Lu	7.19 ± 0.05

Curve IV of the titration plot is the titration of 1:1:2 mixture of Ln, EDDA, and acetylacetone. This titration in comparison with curves I, II, and III allows the estimation of β_1 and β_2 values, as defined previously. The data are shown in Table III. It is noted that in calculating the constants, hydrolysis of the $Ln(EDDA)(H_2O)_n$ complex is usually less than 10% and is not taken into consideration. Because of this approximation, the β_2 values of the heavier lanthanides cannot be determined due to greater extent of system complication by the hydrolysis products.

The β_1 and β_2 values shown in Table III seem to increase with increasing atomic number of lanthanides except for Lu(III). The absolute values of β_1

TABLE III. Mixed Ligand Complex Formation Constants of $Ln(EDDA)(acac)_2^-$ System. $Ln(EDDA)^+ + acac^- \xrightleftharpoons{\beta_1}$ Ln(EDDA)(ACAC) and $Ln(EDDA)^+ + 2acac^- \xrightleftharpoons{\beta_2} Ln(EDDA)(acac)_2^-$

	log β_1	log β_2
La	3.52 ± 0.13	6.71 ± 0.20
Eu	4.50 ± 0.04	7.52 ± 0.40
Er	5.18 ± 0.02	
Yb	5.40 ± 0.12	
Lu	4.96 ± 0.02	

of Ln(EDDA)(acac) systems are greater than those of Ln(DAPDA)(acac) systems. This indicates that the steric effect of the large sized, more shielding DAPDA ligand gives less room for acetylacetonate ion to complex as compared to open-chained ligand, EDDA.

Kinetic Measurements

Attempts were made to study the dissociation kinetics of La, Eu, Er and Yb ternary complexes containing DAPDA or EDDA as primary ligand and acetylacetone as secondary ligand. The complexes were made in solution by mixing appropriate amounts of $Ln(NO_3)_3$, DAPDA·2HCl/EDDA, acac and raising the pH to ~8.0 with Me_4NOH. The complex concentrations were approximately 5×10^{-5} M and ionic strength 0.1 M was adjusted with $LiClO_4$. Both complex and buffer solutions were thermostatted at 25 °C before mixing and the rate of reactions were monitored by change in absorbance due to acetylacetone at 285 nm. A pseudo-first order rate constant of $(2.26 \pm 0.13) \times 10^{-1}$ s^{-1} was obtained for all the complexes studied. Acetic acid–acetate buffers in the pH range 3.72–5.45 were used to study possible acid-dependence on dissociation rates, but the same rate constant was obtained irrespective of acid concentrations in the buffers.

In order to find out if the change in absorbance was due to coordinated acetylacetonate or free acac released after the dissociation of complex; the ternary complexes were made in solution at pH 7 and when they were mixed with acetate buffer of pH 5.45, no significant change in absorbance could be detected. When a solution of acetylacetone (5.0×10^{-5} M) adjusted to pH = 8 with Me_4NOH, was mixed with the above buffer the absorbance at 285 nm decreased with a rate constant of $(2.05 \pm 0.05) \times 10^{-1}$ s^{-1}. Hence, it may be concluded that the dissociation rates of these complexes are too fast to follow on our stopped-flow apparatus, which could measure first-order rate constants up to 2×10^2 s^{-1} only. The changes in absorbance at 285 nm are presumably due to shift in keto–enol equilibrium of free acetylacetone resulting from changes in pH after mixing with buffers.

Unfruitful attempts were also made to study the ternary complex formation kinetics between $La(EDDA)^+$ and acetylacetone. For this study $La(EDDA)^+$ (5.0×10^{-4} M to 5.0×10^{-3} M, pH ~ 8, μ = 0.1) was made in solution by the procedure reported earlier for ternary complexes, and was mixed with acetylacetone (5.0×10^{-5} M in TRIS buffer of pH 7.2). The absorbance at 290 nm grew with a pseudo-first order rate constant of $(3.36 \pm 0.23) \times 10^{-1}$ s^{-1}, which was independent of complex concentration. When this experiment was repeated with the complex solution made in TRIS buffer (pH 7.2), no pronounced change in absorbance at 290 nm could be seen. The outcome of this kinetic study is that the ternary complex formation was complete before the dead time of the instrument and any absorbance change at 290 nm may be because of a shift in keto–enol equilibrium of free acetylacetone.

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