Coordination Tendency of N-Acetylamino Acids, Nucleotides, and DNA toward the Luminescent Bioprobes Tb (III) Bathophenanthroline or Tb (III)-Anthracene-9-Carboxylic Acid

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Abstract
The solid complex Tb (III)-bathophenanthroline (Bphen) was synthesized and characterized by elemental analysis, IR spectra, and thermal analysis. The formation of binary and ternary complexes of Tb(III) with N-acetylamino acids (N-acetylaspartic acid, N-acetylhistidine, and N-acetylhistamine), and Bphen or anthracene-9-carboxylic acid (9-ANCA) has been studied potentiometrically at (25.0(0.1) °C and an ionic strength of I = 0.1mol 3 dm_3. The results obtained confirmed the recognition of the investigated N-acetylamino acids by the luminescent probes used at the molecular level. The formation of binary and ternary complexes of Tb (III) with nucleotides guanosine 50-monophosphate (50-GMP), adenosine 50-monophosphate (50-AMP), cytidine 50-monophosphate (50-CMP), or N-acetylamino acids (N-acetylaspartic acid, N-acetylhistidine, and N-acetylhistamine) has been studied potentiometrically. Confirmation of the formation of the ternary systems of the type Tb(III)-Bphen-N-acetylamino acids or Tb(III)-9-ANCA-N-acetylamino acid in solution has been carried out using UV absorption spectra. The interaction of Tb(III)-Bphen with calf-thymus DNA (CT-DNA) was monitored using electrochemical measurements at a glassy carbon electrode via cyclic voltammetry and square wave voltammetry (SWV) in phosphate buffer (pH 7.00). The data reveal the preferential interaction of Tb (III)-Bphen with the guanine and adenine residues of CT-DNA.

Fluorescence measurements have been carried out to investigate the interaction of Tb(III)-Bphen with CT-DNA and nucleotides 50-GMP, 50-AMP, and 50-CMP.
High-throughput sensing microtiter plate for determination of biogenic amines in seafood using fluorescence or eye-vision†

H. A. Azab, S. A. El-Korashy, Z. M. Anwar, G. M. Khairy, Mark-Steven Steinerb and Axel Duerkop

Abstract

A new optical sensing microplate was developed for rapid screening for the presence of biogenic amines (BAs) in seafood samples with high sensitivity. The deposition of a sensing spot (containing a chameleon dye (Py-1) in a polymeric cocktail) on the bottom of the wells of a standard microplate renders the plate a new sensing tool for a rapid and parallel detection of up to 96 (real) samples. This sensing microplate enables (1) a semi-quantitative readout of analyte concentration by eye-vision, (2) a rapid fluorescence readout of 96 samples with standard instrumentation in less than two minutes (unlike chromatographic and electrophoretic methods), (3) a statistically robust data evaluation (with 8–12 replicates) and (4) a rapid parallel sample preparation with standard 8 or 12-channel micropipettes. On reaction with biogenic amines, the dye shows a significant visible color change from blue over green to red color. The appearance of red color favorably coincides with the concentration of BAs that can induce symptoms of poisoning. The linear ranges of fluorescence calibration data for six biogenic amines cover the clinical toxicological relevant range of BAs that is too low to be detected by the human nose. The LODs range from 0.16 to 0.56 mg mL⁻¹, with correlation coefficients (r²) between 0.985 and 0.999. Finally, the evolution of spoilage of four fish samples (monitored by determination of their BA status) and the increase of their total amine content were found to agree well with previous data on time-dependent evolution of BAs in fish.
Potentiometric, Electrochemical, and Fluorescence Study of the Coordination Properties of the Monomeric and Dimeric Complexes of Eu(III) with Nucleobases and PIPES

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Abstract

The formation of binary and ternary model complexes of Eu(III) with the nucleobases 5-aminouracil (5-amin 2,4-dioxy pyrimidine), dihydrouracil (5,6-dihydro-2,4-dioxy pyrimidine), thymine (2,4-dihydroxy 5-methyl pyrimidine), adenine (6-aminopurine), uracil (2,4-dioxy pyrimidine), and PIPES (piperazine 1,4-bis(2-ethane sulfonic acid) dissodium salt) has been studied potentiometrically at (25.0 (0.1) °C and at an ionic strength of I = 0.1 mol 3 dm_3 (KNO3). The formation of the 1:1, 2:1 binary, and 1:1:1 and 2:1:1 ternary complexes is inferred from the corresponding titration curves. Initial estimates of the formation constants of the resulting species and the protonation constants of the different ligands used have been refined with the SUPERQUAD computer program. The experimental conditions were selected such that self-association of the nucleobases and their complexes was negligibly small; that is, the monomeric and protonated complexes were studied. Recognition of nucleobases and CT-DNA by the luminescent bioprobe Eu(III)_PIPES has been carried out. The solid Eu(III)_PIPES complex was synthesized and characterized using elemental analysis, mass spectra, and IR spectroscopy. The interaction of an aqueous solution of the Eu(III)_PIPES complex with CT-DNA was examined using cyclic voltammetry (CV), differential pulse polarography (DPP), and square wave voltammetry (SWV). The fluorescence emission characteristic band for the Eu(III)_PIPES complex is enhanced by the addition of various concentrations of CT-DNA.
Comparison of the Coordination Tendency of Amino Acids, Nucleobases, or Mononucleotides toward the Monomeric and Dimeric Lanthanide Complexes with Biologically Important Compounds

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Abstract

The formation of monomeric and dimeric binary and ternary complexes of Eu(III), Gd(III), Dy(III), and Pr(III) with primary ligand 2-amino-5-oxy 8-azapurine (8-azaguanine) and amino acids amino-succinic acid (aspartic acid), 2-amino-propanoic acid (D-alanine), (L-alanine), 2-amino-4-methyl thiobutanoic acid (methionine), 2-amino succinic acid (asparagine), 2-amino 4-methyl pentanoic acid (DL-leucine), 2-amino-3-indolyl propanoic acid (L-tryptophan), 2-amino-3-(4-hydroxyphenyl)-propanoic acid (L-tyrosine), 2-amino-3-imidazole propanoic acid (histidine), 2-amino-5-guanidino pentanoic acid (arginine), and 4-amino-5- oxo-pentanoic acid amide (glutamine); or nucleotides adenosine 5-triphosphate (50-ATP), adenosine 5-diphosphate (50-ADP), adenosine 5-monophosphate (50-AMP), adenosine 5-monophosphate (50-GMP), inosine 5-monophosphate (50-IMP), or nucleobases (uracil, 5-aminouracil, dihydrouracil); and with zwitterionic buffers (primary ligands) 4-(2-hydroxyethyl) piperazine- 1-propane sulfonic acid (EPPS), 3-(N-morpholino)-2-hydroxypropane sulfonic acid (MOPSO), 3-(cycloHexylamino)-1-propane sulfonic acid (CAPS), N-(tris(hydroxy methyl)-methyl)-2-amino-ethane sulfonic acid (TES), 3-(cyclohexyl amino)-2-hydroxy-1- propane sulfonic acid (CAPSO), N-(tris(hydroxy methyl)-methyl)-3-amino propane sulfonic acid (TAPS), N-(2-acetamido)-2-a minoethane sulfonic acid (ACES), 2-morpholinoethane sulfonic acid (MES), piperazine 1,4-bis(2-ethane sulfonic acid) (PIPES), N-(1,1-dimethyl-2-hydroxy ethyl)-3-amino 2-hydroxypropane sulfonic acid (AMPSO), N-(2-acetamido)-imino-diabetic acid (ADA); and nucleobases 6-amino-purine (adenine), 2-amino-6-oxypurine (guanine), 2-amino-6-oxy 8-azapurine (8-azaguanine), 5-methyl pyrimidine (thymine), 2,4-dioxypyrimidine (uracil), 5-amino 2,4-dioxypyrimidine (5-aminouracil), and 5,6-dihydro-2,4- dioxypyrimidine (dihydouracil), has been studied potentiometrically at (25.0 (0.1) °C and ionic strength I = 0.1 mol 3 dm−3 (KNO3). The acid_base properties of ligands were investigated and discussed. The formation of the 1:1 and 2:1 binary and 1:1:1 and 2:1:1 ternary complexes are inferred from the corresponding titration curves. The stability constants of the binary and ternary systems were evaluated. Initial estimates of the formation constants of the resulting species and the protonation constants of the different ligands used have been refined with SUPERQUAD computer program.
Synthesis and Fluorescence properties of Eu-anthracene-9-carboxylic acid towards N-acetyl amino acids and nucleotides in different solvents.

H. A. Azab, S. A. El-Korashy, Z. M. Anwar, B.H.M. Hussein, G. M. Khairy

Chemistry Department, Faculty of Science, Suez Canal University

Abstract

Europium (III) complex with Anthracene-9-carboxylic acid (9-AA) has been synthesized and characterized by elemental analysis, FTIR, and TG–DTG techniques. The results indicated that the composition of this complex is Eu (9-AA)₃. The luminescence properties of the complex in different solvents and at different pH values have been investigated. The results show that the complex exhibit more efficient luminescence in THF and ethyl acetate. The interactions of Eu-complex with different N-acetyl amino acids and nucleotides in different solvents have been investigated by fluorescence measurements. Enhancement of the fluorescence intensities has been observed in cyclohexane, acetone, acetonitrile, and tetrahydrofuran whereas the fluorescence intensities of the investigated complex in ethanol, water, and ethyl acetate exhibit relatively low intensity.
Pyrimidine and Purine Mononucleotides Recognition by Trivalent Lanthanide Complexes with N-Acetyl Amino Acids

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Abstract

Potentiometric equilibrium measurements have been performed at (25.0 (0.1) °C and ionic strength I ) 0.1 mol -dm-3 KNO3 for the interaction of the biologically important ligands N-acetyl histidine, N-acetyl L-leucine, N-acetylglutamic acid, N-acetylhistamine, N-acetylaspartic acid. and La(III), Gd(III), Sm(III), Tb(III), Eu(III), and Dy(III) with the nucleotides guanosine 5′-monophosphate (5′-GMP), cytidine 5′-monophosphate (5′-CMP), inosine 5′-monophosphate (5′-IMP), adenosine 5′-monophosphate (5′-AMP), adenosine 5′-diphosphate (5′-ADP), adenosine 5′-triphosphate (5′-ATP), and cytidine 5′-triphosphate (5′-CTP) in 1:1:1 and 1:2:1 ratios. The formation constants of various mixed ligand complexes were inferred from the potentiometric titration curves. Initial estimates of the formation constants of the resulting species and the formation constants of the different N-acetyl amino acid (NAA) and nucleotide (NU) complexes in metal ligand ratios 1:1 and 2:1 have been refined with the SUPERQUAD computer program. Confirmation of the formation of binary and ternary complexes of the type Ln(III)-NU-NAA and the possible recognition of the purine and pyrimidine mononucleotides by N-acetyl amino acid complexes of lanthanides in aqueous media have been carried out using UV spectroscopic and fluorimetric measurements.
Ternary Complexes of La(III), Ce(III), Pr(III) or Er(III) with Adenosine 5_-mono, 5_-di, and 5_-triphosphate as Primary Ligands and some Biologically Important Zwitterionic Buffers as Secondary Ligands

Adel S. Orabi · Hassan A. Azab · F. Saad · Hani Said

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Abstract

Equilibrium constant measurements have been performed potentiometrically at (25 ± 0.1) °C and an ionic strength \( I = 0.1 \) mol · dm⁻³ KNO₃ for the interaction of La(III), Ce(III), Pr(III) and Er(III) with the purine nucleotides adenosine 5_-mono, 5_-di, and 5_-triphosphate and with the biologically relevant secondary ligand zwitterionic buffers 3-(cyclohexyl amino)-1-propanesulfonic acid (CAPS), 3-(cyclohexylamino)-2-hydroxy- 1-propane sulfonic acid (CAPSO), N-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS), 3-(N-bis(hydroxyethyl)amino)-2 hydroxypropanesulfonic acid (DIPSO), N,Nbis( 2-hydroxyethyl)glycine (BICINE), and N-(2-acetamido)-2-iminodiacetic acid (ADA) in a 1:1:1 ratio. The formation of various 1:1:1 normal and protonated mixed-ligand complex species was inferred from the potentiometric pH titration curves. The experimental conditions were selected such that self-association of the purine nucleotides and their complexes was negligibly small; that is, the monomeric normal and protonated ternary complexes were studied. Initial estimates of the formation constants of the resulting species and the acid dissociation constants of adenosine 5_-mono-, 5_-di-, and 5_-triphosphate and the zwitterionic buffer secondary ligands were refined with the Superquade computer program. In some Ln(III) mixed-ligand systems, interligand interactions between the coordinating ligands, possibly involving H-bond formation, have been found to be the most important factors in deciding the stability of the mixed-ligand complexes in solutions. The thermodynamic \( _{\text{G}}G^\circ \) values of the monomeric normal and protonated ternary complexes were calculated and discussed.

Keywords Zwitterionic buffer · Purine nucleotides · Formation constants · Binary and ternary complexes · Lanthanide ion · Thermodynamic
Fluorescence and Electrochemical Probing of N-Acetylamino Acids, Nucleotides, and DNA by the Eu(III)-Bathophenanthroline Complex†

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Abstract

The solid complex Eu(III)-bathophenanthroline was synthesized and characterized by elemental analysis, IR spectra, and thermal analysis. The interaction of the Eu(III)-bathophenanthroline solid complex with calf-thymus DNA has been investigated by fluorescence and electrochemical methods including cyclic voltammetry and differential pulse polarography on a glassy carbon electrode. The formation of binary and ternary complexes of Eu(III) with nucleotides guanosine 5′-monophosphate (5′-GMP), adenosine 5′-monophosphate (5′-AMP), inosine 5′-monophosphate (5′-IMP), cytidine 5′-monophosphate (5′-CMP), or N-acetylamino acids (N-acetylaspartic acid, N-acetylhistidine, and N-acetylhistamine), and bathophenanthroline (BPhen) has been studied potentiometrically at (25.0 ± 0.1) °C and an ionic strength of I = 0.1 mol · dm⁻³ (KNO₃) in 1.8 % v/v ethanol-water mixture solvent. The formation of the normal and protonated binary and ternary complexes is inferred from the corresponding titration curves. The experimental conditions were selected such that self-association of the nucleotides and their complexes was negligibly small, that is, the monomeric complexes were studied. Initial estimates of the formation constants of the resulting species and the protonation constants of the different ligands used have been refined with the SUPERQUAD computer program. Confirmation of the formation of the ternary systems of the type Eu(III)-bathophenanthroline-N-acetylamino acids or nucleotides in solution has been carried out using UV-visible, cyclic voltammetry, square wave voltammetry, and emission spectrofluorometric measurements.
Eu(III)-Anthracene-9-carboxylic Acid as a Responsive Luminescent Bioprobe and Its Electroanalytical Interactions with N-Acetyl Amino Acids, Nucleotides, and DNA

Chemistry Department, Faculty of Science, Suez Canal University, Ismailia 41522, Egypt

Abstract

The interaction of Eu(9-ANCA)3 (9-ANCA ) anthracene-9-carboxylic acid) with DNA has been investigated by a fluorescence method. Potentiometric equilibrium measurements have been performed at (25.0 ( 0.1) °C and ionic strength ) 0.1 mol · dm-3 KNO3 for the interaction of Eu(III) and 9-ANCA with adenosine5′-diphosphate (ADP), adenosine 5′-triphosphate (ATP), N-acetyl glutamic acid (Nc-Glu), N-acetyl leucine (Nc-Leu), and N-acetyl lysine (Nc-Lys) in a 1:1:1 ratio. The formation of various mixed ligand complexes was inferred from the potentiometric titration curves. The formation constants of the binary and ternary complexes have been refined with the SUPERQUAD computer program. The interaction of Eu(III)-(9-ANCA) with Nc-Glu, Nc-Leu, and Nc-Lys has been investigated by electroanalytical methods including cyclic voltammetry (CV), differential pulse polarography (DPP), and square wave voltammetry (SWV) on a glassy carbon (GC) electrode.
Upconverting nanoparticle based optical sensor for carbon dioxide

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Abstract

We demonstrate a novel optical sensor for carbon dioxide in concentrations between 0 and 3%. The sensing scheme is based on the optical interrogation of a 12_μm polystyrene (PS) film containing upconverting nanoparticles (UCNP; 40–100nm in size) of the type NaYF4:Yb,Er, and the longwave absorption pH probe bromothymol blue (BTB) in its anionic (blue) form. PS is chosen as a matrix because it displays permeation selectivity for CO2 and rejects protons. The color of BTB in the PS matrix depends on the partial pressure of CO2 gas. The UCNPs are photoexcited with a 980-nm laser diode to give a green (542 nm) and a red (657 nm) emission whose intensity is screened off (depending on whether BTB is present in its blue or yellow form) due to an inner filter effect. The luminescence intensities of the UCNPs at 542nm and 657nm increase with increasing concentration of CO2. The pH probe BTB (a sulfonate) is used in the form of a lipophilic ion pair with the tetrabutylammonium cation (TBA). The strong base tetraoctylammonium hydroxide is added to the system and acts as a base to convert BTB in its phenoxide (blue) form, but also creates a buffer system. This is the first optical sensor for CO2 that is based on the use of UCNPs. Its response time is ~10 s on switching from pure argon gas to 1% CO2 in argon, the recovery time of the sensing film is ~180 s, and the detection limit is 0.11% of CO2.
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Upconverting nanoparticle based optical sensor for carbon dioxide


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