

Activation energies of intermolecular dynamics in ethylenediaminetetraacetate complexes with lanthanides: An effect of the “gadolinium break”



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ABSTRACT

Earlier the monotonic increase of the free energy of chemical exchange processes along the series of lanthanide $[\text{Ln}(\text{H}_2\text{O})_n(\text{EDTA}^{4-})]^-$ complexes was found [Babailov S.P., *Magnet. Reson. Chem.*, **2012**, 50, 12, 793] for the yttrium subgroup (Tb^{3+} , Ho^{3+} , Tm^{3+} , Yb^{3+} and Lu^{3+}). In the present paper ^1H NMR measurements are reported for the aqueous solutions of $[\text{Ln}(\text{H}_2\text{O})_n(\text{EDTA}^{4-})]^-$ complexes of the cerium subgroup (La^{3+} (**I**), Pr^{3+} (**II**) and Eu^{3+} (**III**); $n = 1, 2$ and 3). It is determined that the activation free energies (ΔG_{298}^\ddagger) of the intermolecular EDTA^{4-} ions exchange at $[\text{Ln}(\text{H}_2\text{O})_n(\text{EDTA}^{4-})]^-$ complexes are 65 ± 3 , 65 ± 3 and 64 ± 3 kJ/mol for **I**, **II** and **III** respectively (at $\text{pD} = 2.5$). Comparison ΔG_{298}^\ddagger values for the light and the heavy lanthanides showed a “gadolinium break” of the dependence of the ΔG_{298}^\ddagger on the lanthanide cation numbers. The obtained results indicate that coordination compounds **II** and **III** may be considered as thermometric NMR sensor and lanthanide paramagnetic probes for *in situ* temperature control in solution.

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1. Introduction

The paramagnetic aminopolycarboxylate compounds of lanthanides (Ln) attract the interest of researchers due to numerous practical applications (as relaxation contrast agents for MRI, agents for photodynamic therapy, fluorescent and NMR probes, etc.) [1–6]. EDTA^{4-} complexes with Ln are one of the varieties of this type of coordination compounds. Lanthanide-(EDTA^{4-}) complexes have also many applications (in particular lanthanide and actinide separation of spent fuel nuclear power plants) [7,8]. They are studied in detail by various methods (see discussion and Refs. in [7,9]). Recently, we in particular investigated the intramolecular dynamics related to interconversion of $\Delta\text{-}\lambda_{\text{E}}\text{-}\delta\delta\delta\delta$ and $\Delta\text{-}\delta_{\text{E}}\text{-}\delta\delta\delta\delta$

conformers with estimated activation free energy $\Delta G^\ddagger(298\text{ K}) = 50 \pm 4$ kJ/mol [9]. It should be noted that the energy characteristics of the kinetics of intermolecular dynamics studies are incomplete. We previously reported on monotonic variation of the free energy of activation Ln association with EDTA^{4-} as an example of the lanthanide yttrium subgroup [10], although the cerium subgroup of these characteristics still remain unexplored. In this regard, the objectives of the work were to analyze the kinetics of chemical exchange (CE) processes between EDTA^{4-} in two states (free and coordinated with lanthanide cations) within the lanthanide series.

It is known that the properties of the Ln complexes of the first half of the series can be different from the properties of the complexes of the second half of the homologous series [1,5,11]. This variation often occurs between the Eu and Tb elements (which may be regarded as the “gadolinium break”) [1,5,11]. This can manifest itself in a change of the molecular structure, thermodynamic stability, the paramagnetic properties, etc. Thus, for example, by reacting the compounds $[\text{Ln}(\text{NO}_3)_3]$ or $[\text{LnL}_3]$ with 18-crown-6 in solution in the case of the cerium subgroup formed the complexes $[\text{Ln}(18\text{-crown-6})(\text{NO}_3)_3]$ [5,12], and $[\text{Ln}(18\text{-crown-6})]$

Abbreviations: EDTA^{4-} , ethylenediaminetetraacetate anion; DTPA, diethylenetriaminepentaacetic acid; H_4DOTA , 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid; MRI, magnetic resonance imaging; NMR, nuclear magnetic resonance; DNMR, dynamic NMR; CE, chemical exchange; Ln, lanthanide cations; LIS, lanthanide-induced shift.

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6)L₂]⁺ respectively [5] (here L is 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione). The lanthanide cation forms coordination bonds with all electron-donor hetero-atoms of the crown ether molecule in all of these complexes. However, these types of complexes were not detected in the case of yttrium subgroup. In the paper, the “gadolinium break” of physicochemical properties discovered for the first time by the example of the changing nature of dependence of the free energy of activation of the intermolecular dynamics on the lanthanide cation numbers. To this end, we studied the NMR spectra of lanthanide complexes with EDTA⁴⁻ depending on temperature and pD. ¹H NMR measurements are reported for the aqueous solutions of EDTA⁴⁻ complexes of La³⁺ (I), Pr³⁺ (II) and Eu³⁺ (III). The found results are in particular useful for understanding solution chemistry of lanthanides with EDTA⁴⁻, which is applicable to lanthanide–lanthanide separations and actinide/lanthanide behavior in storage pond conditions within the area of nuclear waste management [1,5,11]. The obtained temperature dependences of paramagnetic lanthanide-induced shifts (LISs) indicate that coordination compounds II and III may be considered as thermometric NMR sensor and lanthanide paramagnetic probes for *in situ* temperature control in solution.

2. Results and discussion

2.1. ¹H NMR signal assignment in [Ln(H₂O)_n(EDTA⁴⁻)]⁻ complexes

The ¹H NMR experimental study of Na[Eu(EDTA⁴⁻)] complexes in aqueous solution indicates the formation of thermodynamically stable Ln-(EDTA⁴⁻) complexes (Fig. 1). The chemical shift values of hydrogen atoms of inequivalent CH₂ groups in the ¹H NMR spectra of III complex have substantial paramagnetic lanthanide-induced contributions { $\delta = 2.3$ (N-CH₂-CH₂-N fragment), 0.9 (N-CH₂-COO) and -2.0 (N-CH₂-COO) ppm at $T = 367$ K, pD = 2.5}. One can find in the spectra both the signals of free and the Ln coordinated EDTA⁴⁻ anions at low temperature and a pD range from 1 to 9. The signals of free EDTA⁴⁻ anions with chemical shifts $\delta = 3.57$ and 3.19 ppm (Fig. 1) are observed in the spectra simultaneously with the signals corresponding to the associated EDTA⁴⁻ anions of [Ln(H₂O)_n(EDTA⁴⁻)]⁻ complexes (at pD = 2.5 and temperature from 293 to 323 K; $n = 1, 2$ and 3).

This indicates that rapid (in the NMR scale) CE between nonassociated and associated EDTA⁴⁻ anions is absent at low temperature. According to our calculations (taking into account the distribution diagrams), the abundance of the [Eu(H₂O)_n(EDTA⁴⁻)]⁻ complex is only 70% and there are 20% of the protonated form [EuD(H₂O)_n(EDTA⁴⁻)] and near 10% of free Eu(III) at pD = 2.5. It can be expected in this case that of the free ligand will be about 10%. We conducted a study of the integrated intensities of the signals in order to test this thesis. We experimentally found (from analysis of the integrated intensities of NMR signals) that the abundance of free EDTA⁴⁻ anions is $9 \pm 1\%$ at 293 K (Fig. 1). It is in accordance with calculations. The observed reducing the value of paramagnetic lanthanide-induced shifts for the CH₂ groups at temperature decrease (from 333 to 293 K) is due to both changes in the ratio of concentrations [Eu(H₂O)_n(EDTA⁴⁻)]⁻ and [EuD(H₂O)_n(EDTA)] by shifting the equilibrium and the influence of the number of water molecules associated [22–24]. It should be noted for a discussion that from the point of view of thermodynamics the Eu/(EDTA⁴⁻) system at a ratio of 1:1 may have a more complicated character. It was indicated earlier by the excitation spectra formation [Eu(H₂O)₃(EDTA⁴⁻)]⁻ {CN = 9} and [Eu(H₂O)₂(EDTA⁴⁻)]⁻ {CN = 8} in aqueous solution. These complexes are characterized by an average lifetime of 318 μ s and effective NH₂O = 2.6 [22]. Formation the [Eu(H₂O)₃(EDTA⁴⁻)]⁻ complex was also determined by X-ray data in the crystal state (see in particular the project AZEBAL from the Cambridge database). It is possible that the system is characterized by the thermodynamic equilibrium between the four main components.

It can be mentioned that the formation of I–II complexes was also experimentally found here by ¹H NMR in the entire temperature range studied (from 273 to 368 K) and in a pD range from 1 to 9.

2.2. Intermolecular dynamics

The ¹H NMR spectra of III (useful for D NMR analysis) are given in the Fig. 2. These spectra are more detailed than those presented at the Fig. 1. The most intense one belongs to residual hydrogen atoms of deuterium enriched heavy water (with chemical shift $\delta = 4.8$ ppm). It should be noted that with increasing temperature, a change in the shape of NMR signals corresponding to hydrogen atoms of CH₂ groups of free EDTA⁴⁻ anions is observed, which is

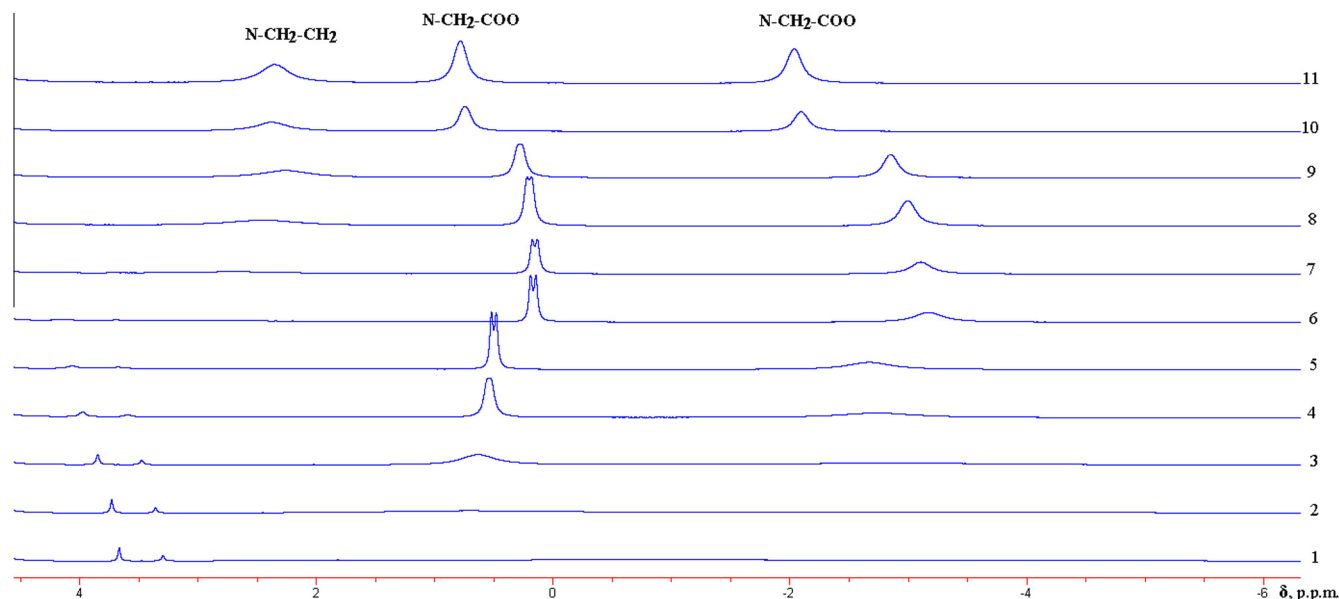


Fig. 1. Variable temperature dependence of 400 MHz ¹H NMR spectra of [Eu(H₂O)_n(EDTA⁴⁻)]⁻ in D₂O (pD = 2.5 ± 0.1, initial concentration of Na[Eu(EDTA⁴⁻)] c = 0.01 M) at temperatures (T, K): 278 (1), 283 (2), 293 (3), 303 (4), 313 (5), 323 (6), 333 (7), 343 (8), 353 (9), 363 (10), 367 (11).

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