

Potentiometric Determination of the Stability Constants of Lanthanide Complexes with Iminodiacetic Acid in Water and Dioxane-Water Mixtures

Sevgi ARZİK, Ebru MAVİOĞLU AYAN and A. Sedat ÇELEBİ*

Department of Chemistry, Faculty of Science, Ege University, Bornova,

35100, İzmir-TURKEY

e-mail: ascelebi@ttmail.com

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The protonation constants of iminodiacetic acid (H_2ida) and the stability constants of its complexes with Nd(III), Sm(III), Gd(III), Dy(III), and Er(III) ions at metal/ligand mole ratios of 1:1, 1:2, and 1:3 at 25 °C and 0.1 M ionic strength in aqueous medium and 20%, 45%, and 70% w/w dioxane-water mixtures were determined by the potentiometric method using the BEST computer program. The stability constants of the complexes that formed increased as the dioxane content increased. The stability of all the analogues' complexes, both in aqueous medium and in dioxane-water mixtures, were in the order of Nd(III) < Sm(III) < Gd(III) < Dy(III) < Er(III).

Key Words: Iminodiacetic acid, lanthanide(III) complexes, stability constants, dioxane-water mixtures.

Introduction

Iminodiacetic acid (H_2ida), a well-known aminopolycarboxylic acid, is one of the most widely used complexing agents in industry.

It has been generally reported as a dibasic acid;¹ however, at pH < 2.5 a third protonation of iminodiacetic acid begins to play a significant role.²⁻⁴ The complete dissociation equilibria are, therefore, as in Figure 1.

It is difficult for ligands that only contain nitrogen donor atoms to bind to lanthanide ions in aqueous media, as expected according to the HSAB rule; however, the coordination properties of neutral nitrogen atoms toward lanthanides are strongly enhanced when negatively charged oxygen donors are also present in the ligands.⁵ The dianionic form of iminodiacetic acid, ida^{2-} , therefore, acts as a terdentate chelating agent in aqueous solutions.⁶

Some X-ray crystallographic studies have elucidated that the same coordination mode is also valid in solid ida complexes.^{7,8} A recent study has shown that it functions as a pentadentate ligand in a Ce(III)- ida coordination polymer.⁹

*Corresponding author

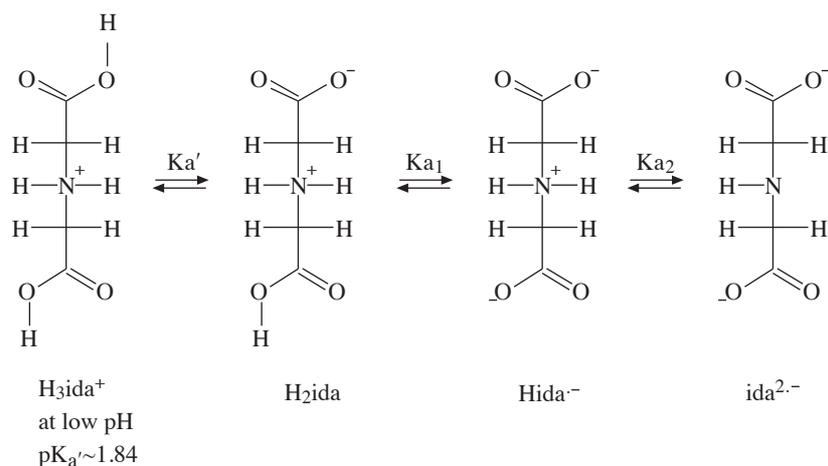


Figure 1. Dissociation equilibria of iminodiacetic acid.

To the best of our knowledge the literature contains no studies regarding the stability constants of lanthanide complexes with iminodiacetic acid in dioxane-water mixtures; however, 2 comprehensive reviews have given the stability constants of 1:1 and 1:2 complexes in aqueous medium at 25 °C and 0.1 M ionic strength.^{10,11}

The ionic radii of trivalent lanthanide ions are similar to the ionic radius of calcium ion; therefore, Ca^{2+} and the lanthanide ions react with aminopolycarboxylates in a similar manner;¹ but the formation constants of lanthanide complexes are considerably larger than those of Ca^{2+} complexes ($\log K_1 = 2.6$ for Ca^{2+} , 5.9 for La^{3+} , and 7.5 for Lu^{3+} for ida complexes)¹¹ primarily for 3 reasons. First, the higher charge/radius ratios lead to stronger electrostatic bonding. Secondly, the lanthanide ions have a larger hydration sphere than Ca^{2+} . Replacement of many water molecules by a few molecules of the ligand increases the entropy of the systems, which in turn results in higher stability constants. An additional factor is the ability of Ln^{3+} ions to accommodate more ligands than calcium.¹¹

It has been implied in the above-mentioned reviews that 1:3 complexes, $\text{Ln}(\text{ida})_3^{3-}$, have not formed; however, $\text{Eu}(\text{ida})_3^{3-}$ has been reported in 2 publications.^{6,12}

One of the main purposes of the present study was to confirm the presence of 1:3 complexes of lanthanide(III) ions with iminodiacetic acid and to compute their stability constants. Another aim was to examine the nature of the bonding between lanthanide(III) ions and the ligand through the investigation of the effect of the dielectric constant of the medium upon the stability constants. Five other lanthanides (Nd, Sm, Gd, Dy, and Er) were chosen to observe the variation along the series; water, and 20%, 45%, and 70% w/w 1,4-dioxane-water mixtures were used as reaction media.

Experimental

Materials

All chemicals were analytical reagent grade. Iminodiacetic acid (Aldrich) and hydrated lanthanide nitrates (Strem and Sigma) were used without further purification. Lanthanide solutions were acidified with accurately known amounts of HNO_3 to prevent hydrolysis. The exact concentrations of the solutions of the lanthanide nitrates were determined by complexometric titration with disodium salt of EDTA, using EBT

indicator. Dioxane (99%) was purchased from Merck and further purified accordingly.¹³

All solutions were prepared in doubly distilled CO₂-free water. Carbonate-free KOH was standardized by titration with pure potassium hydrogen phthalate. HNO₃ solution was standardized with KOH according to Gran's method.¹⁴

Apparatus

A Jenway 3040 ion analyzer with a combined glass electrode (Mettler) was used to determine hydrogen ion concentrations. A 0.100 M KCl-filled reference electrode was employed for mixed solvent studies, in contrast to use of saturated KCl solution for aqueous solutions.¹ Potentiometric titrations were performed in a specially designed glass cell equipped with a magnetic stirrer. Temperature was controlled by circulation of thermostated water through the jacket. All titrations were performed under CO₂-free nitrogen, which was pre-saturated with the solvent, identical to that of the corresponding reaction prior to entering the reaction vessel.

Potentiometric titrations

Iminodiacetic acid generally coordinates to metal ions in dianionic form, that is, complexation is a proton-releasing reaction. Therefore, the experimental method consisted of potentiometric titration of the ligand in the absence and presence of lanthanide ions.

As is known, pH-meters read $-\log a_{H^+}$ (pH), whereas the potentiometric method we used for the calculation of stability constants requires $-\log[H^+]$ (p[H]). Hence, the first step in computations was to obtain calibration curves (straight lines) giving p[H]s against measured pH values for each solvent medium. This was accomplished by titrating dilute HNO₃ solutions (to ensure the constancy of the ionic strength and to avoid errors stemming from junction potential differences) with a standard KOH solution.¹ At first the pH-meter was set to read $-\log[H^+]$ and $[H^+]$ was calculated from the initial data.

Dioxane-water solvents were treated just like aqueous solutions for potentiometric purposes.¹ pK_w^c values valid for 25 °C and 0.1 M ionic strength were computed via the Debye-Huckel equation for water, and 20%, 45%, and 70% w/w dioxane-water mixtures.¹⁵ pK_w values and the data required for the related calculations (dielectric constants and densities) were obtained from Harned and Owen.¹⁶

The initial total volume of the solution in the reaction vessel was always 50.0 mL. The concentration of iminodiacetic acid was 5.0×10^{-3} M in each case and that of lanthanide was based on the starting ligand to metal ratio. The acid present in the lanthanide stock solution to prevent hydrolysis was calculated and introduced into the BEST program as excess acid.

The temperature was kept constant at 25 ± 0.05 °C and ionic strength was maintained at 0.1 M using KNO₃ solution throughout each titration.

No turbidity was observed at any stage during the course of each titration.

Calculation of stability constants

The protonation constants of iminodiacetic acid and the stability constants of its lanthanide complexes were computed via the BEST computer program.¹ Species distribution diagrams of the ligand-metal systems were drawn using the SPE program.¹

Although a single titration of a solution having a 1:3 molar ratio of metal to ligand theoretically suffices to obtain all 3 stepwise stability constants, a step-by-step procedure was utilized for the sake of accuracy. The stability constant of the 1:1 complex, $Ln(ida)^+$, was calculated first from the titration data of a solution with a 1:1 molar ratio of metal to ligand. When the titration data of the solution with a 1:2 molar ratio of metal to ligand was used to compute the stability constant of the 1:2 complex, $Ln(ida)_2^-$, the first value was then entered into the pertinent file as an input, and so on. The BEST program actually computes the overall stability constants. The stepwise constants were then obtained accordingly.

The standard deviations of the overall stability constants were calculated using the method reported by Olivieri and Escandar.¹⁷

Results and Discussion

In the pH range we worked with only the first 2 protonations of iminodiacetic acid played a significant role. Hence, their constants were determined potentiometrically, as explained previously, and are given in Table 1.

Table 1. Protonation constants of iminodiacetic acid in different solvent media at 25 °C and I = 0.1.

Protonation constant ^a	Aqueous medium	20% (w/w) dioxane-water	45% (w/w) dioxane-water	70% (w/w) dioxane-water
$\log \beta_{HL}$	9.47 ± 0.01	9.95 ± 0.01	10.90 ± 0.01	12.00 ± 0.01
$\log K_1^H$	9.47	9.95	10.90	12.00
$\log \beta_{H_2L}$	12.15 ± 0.01	12.85 ± 0.01	14.65 ± 0.01	16.20 ± 0.01
$\log K_2^H$	2.68	2.90	3.75	4.20

^a : \pm values are standard deviations

The values calculated for the aqueous medium are in good agreement with those given by other researchers ($\log K_1^H = 9.33^{10}$ and 9.34^{11} and $\log K_2^H = 2.58^{10}$ and 2.55^{11} as compared to our values of 9.47 and 2.68). No constants have been reported for dioxane-water mixtures.

It has been stated that at up to an approximately 50% organic solvent concentration in organic solvent-water mixtures the electrostatic effect predominates and $\log K_H$ of a ligand varies almost linearly with the reciprocal of the dielectric constant.¹⁸ Upon addition of dioxane more water molecules are replaced by organic molecules. As the basicity of dioxane is lower than that of water, this non-electrostatic effect seems to decrease the proton-accepting property of the mixed solvent, as a whole; however, dioxane molecules progressively break down the H-bonded structure of water and this second non-electrostatic effect counteracts the first one, with respect to the proton acceptance property of the media. These considerations have been reflected in the deviation from linearity of $\log K_1^H(pK_{a2})$ and $\log K_2^H(pK_{a1})$ plotted against $100/D$ in Figure 2. Plotting protonation constants against the mole fraction of dioxane will give results similar to those in Figure 2.

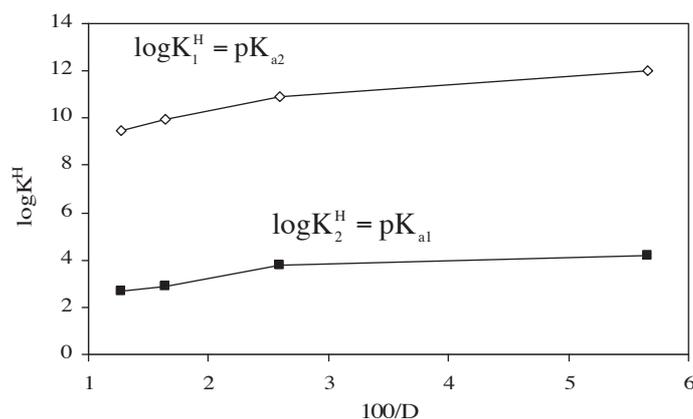


Figure 2. Protonation constants of iminodiacetic acid vs. $100/D$ at $25\text{ }^\circ\text{C}$ and $I = 0.1$; (D) as the dielectric constant of the medium.

To be sure that complexation really occurred, titration curves for the strong acid, ligand, metal, and metal + ligand were first plotted in the same figure (Figure 3).¹⁹ It reveals some significant points regarding this ligand + metal system. The ligand titration curve was displaced from that of the strong acid around pH 8 due to the third dissociation of iminodiacetic acid. The metal titration curve departed from that of acid at about pH 6.5 because of the hydrolysis of lanthanide ions. The titration curve of metal + ligand was displaced from that of the ligand at about pH 3, which confirms formation of the complex.

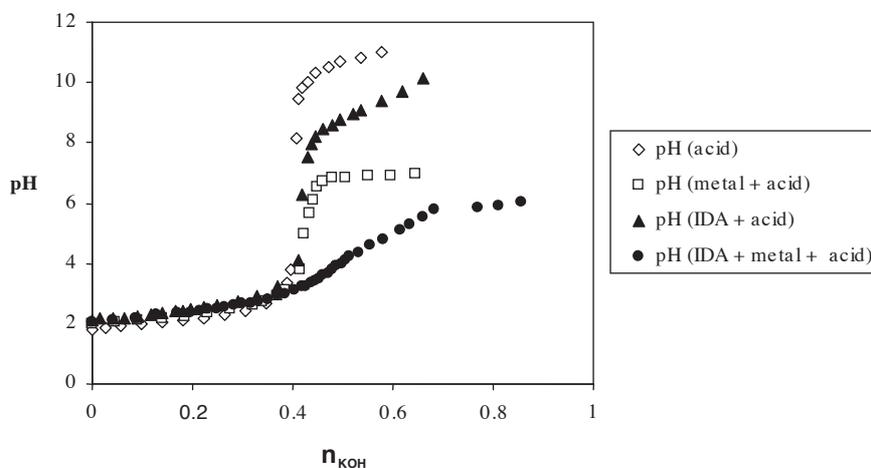


Figure 3. Representative titration curves for the strong acid (0.01 M HNO_3), ligand ($0.005\text{ M HNO}_3 + 0.005\text{ M H}_2\text{ida}$), metal ($0.01\text{ M HNO}_3 + 0.005\text{ M Dy}^{3+}$), and metal + ligand ($0.005\text{ M HNO}_3 + 0.005\text{ M H}_2\text{ida} + 0.005\text{ M Dy}^{3+}$) at $25\text{ }^\circ\text{C}$ and $I = 0.1$ in aqueous solution.

Titration data for 5 solutions with different concentrations ($6.25 \times 10^{-4}\text{ mol/L}$ – $1.00 \times 10^{-2}\text{ mol/L}$) for each metal-ligand system with a 1:1 molar ratio of ligand to metal were assessed to test for the possibility of any polynuclear complexes. The values obtained were independent of concentration, which strongly suggests that only mononuclear complexes formed.^{1,20}

Some computational tests using BEST were performed to verify the formation of any hydrolysis products ($\text{Ln}(\text{ida})(\text{OH})$, $[\text{Ln}(\text{ida})_2(\text{OH})]^{2-}$, etc.) or protonated complexes ($\text{Ln}(\text{Hida})^{2+}$, $\text{Ln}(\text{Hida})(\text{ida})$,

etc.).³ Some tentative $\log\beta$ values for the assumed species were introduced into the input file. None of these assumed complexes resulted in a good fit and proved a predominant species.

The stability constants of 1:1, 1:2, and 1:3 complexes in water and dioxane-water mixtures are given in Table 2. As expected, 3 stepwise stability constants in water and dioxane-water mixtures increased along the series (Figure 4). A discontinuity at gadolinium (the gadolinium break) has been observed, to some

Table 2. Stability constants of the lanthanide complexes with iminodiacetic acid in water and dioxane-water mixtures at 25 °C and $I = 0.1$.

Stability constants ^a	Aqueous solution	20% w/w dioxane-water	45% w/w dioxane-water	70% w/w dioxane-water
ida-Nd				
$\log\beta_1 = \log K_1$	6.60 ± 0.01	7.41 ± 0.01	8.79 ± 0.01	10.50 ± 0.02
$\log\beta_2$	11.62 ± 0.01	13.24 ± 0.02	15.80 ± 0.02	20.03 ± 0.02
$\log K_2$	5.02	5.83	7.01	9.53
$\log\beta_3$	14.87 ± 0.03	16.64 ± 0.03	19.60 ± 0.02	25.10 ± 0.03
$\log K_3$	3.25	3.41	3.80	5.07
ida-Sm				
$\log\beta_1 = \log K_1$	6.78 ± 0.02	7.60 ± 0.01	9.00 ± 0.02	10.80 ± 0.03
$\log\beta_2$	12.00 ± 0.02	13.79 ± 0.03	16.60 ± 0.02	20.54 ± 0.03
$\log K_2$	5.22	6.19	7.60	9.74
$\log\beta_3$	15.53 ± 0.02	17.76 ± 0.02	21.10 ± 0.03	26.30 ± 0.03
$\log K_3$	3.53	3.87	4.50	5.76
ida-Gd				
$\log\beta_1 = \log K_1$	6.80 ± 0.01	7.63 ± 0.01	9.11 ± 0.01	10.98 ± 0.02
$\log\beta_2$	12.15 ± 0.01	13.91 ± 0.03	16.89 ± 0.02	20.88 ± 0.02
$\log K_2$	5.35	6.28	7.78	9.90
$\log\beta_3$	15.80 ± 0.02	17.95 ± 0.05	21.89 ± 0.03	26.88 ± 0.02
$\log K_3$	3.65	4.04	5.00	6.00
ida-Dy				
$\log\beta_1 = \log K_1$	6.95 ± 0.01	7.82 ± 0.01	9.39 ± 0.01	11.20 ± 0.01
$\log\beta_2$	12.48 ± 0.01	14.44 ± 0.02	17.64 ± 0.02	21.31 ± 0.02
$\log K_2$	5.53	6.62	8.25	10.11
$\log\beta_3$	14.48 ± 0.02	18.83 ± 0.03	23.14 ± 0.02	27.99 ± 0.02
$\log K_3$	4.00	4.39	5.50	6.68
ida-Er				
$\log\beta_1 = \log K_1$	7.15 ± 0.01	8.00 ± 0.01	9.64 ± 0.01	11.39 ± 0.02
$\log\beta_2$	12.85 ± 0.01	14.85 ± 0.02	18.44 ± 0.02	21.68 ± 0.02
$\log K_2$	5.70	6.85	8.80	10.29
$\log\beta_3$	17.13 ± 0.02	19.54 ± 0.02	24.29 ± 0.02	28.96 ± 0.03
$\log K_3$	4.28	4.69	5.85	7.28

^a: Values are expressed as \pm SD.

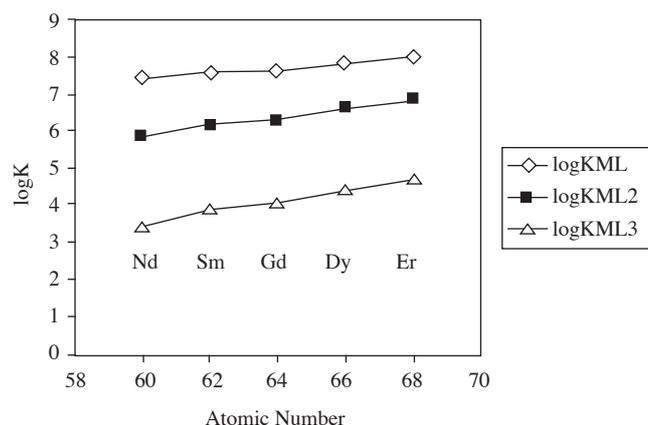


Figure 4. Variation of the stepwise stability constants of iminodiacetic acid complexes of lanthanides, with atomic numbers (in 20% w/w dioxane-water mixture).

extent.²¹ Similar profiles have been obtained when stability constants were plotted against z^2/r of lanthanide ions. To the best of our knowledge there are no studies regarding the stability constants of lanthanide complexes with iminodiacetic acid in dioxane-water mixtures in the literature. The values reported for the stability constants of 1:1 and 1:2 complexes in aqueous solution are in good agreement with what we observed in the present study.^{10,11} The presence of a 1:3 europium complex with iminodiacetic acid, $Eu(ida)_3^{3-}$, has been reported.^{6,12} In one of these reports it was suggested that even the third ida^{2-} behaves as a tridentate chelating ligand, replacing 3 coordinated water molecules.¹² The findings of the second article imply that the third ida^{2-} coordinates to the metal ion in a bidentate fashion, in contrast to the first two.⁶ We observed that K_3/K_2 is considerably lower than K_2/K_1 (this discrepancy becomes more pronounced in dioxane-water mixtures), which seems to support the fact that the third ida^{2-} acts in a bidentate manner.

A representative species distribution curve is given in Figure 5.

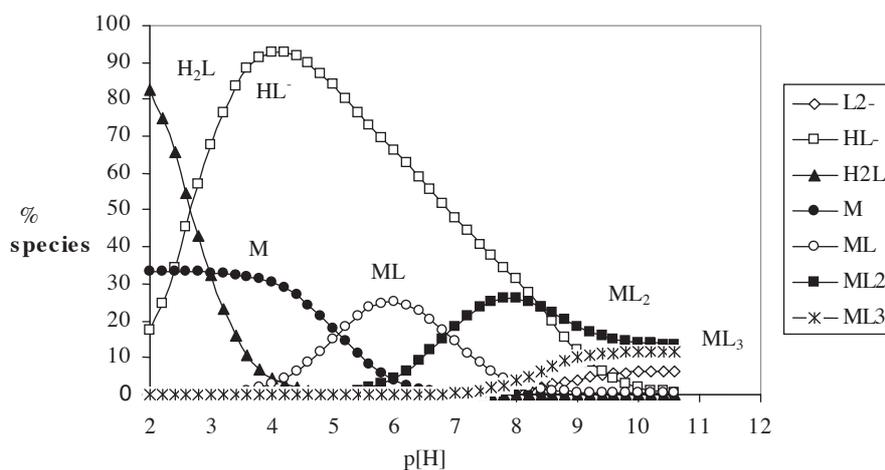


Figure 5. Species distribution curves for Sm- H_2ida (1:3) at 25 °C and $I = 0.1$ M ionic strength in aqueous solution.

The stability constants of the lanthanide complexes with iminodiacetic acid increased as the dielectric constant of the medium decreased (with an increase in the percentage of dioxane in the medium), as expected, because the interaction between a lanthanide ion and a ligand is mainly electrostatic (Figure

6).²²⁻²⁴ Variation was almost linear, up to about the 50% dioxane concentration, the electrostatic effect predominated. Over about the 50% dioxane concentration non-electrostatic effects, as stated regarding protonation constants, became more pronounced and caused some deviation from linearity.

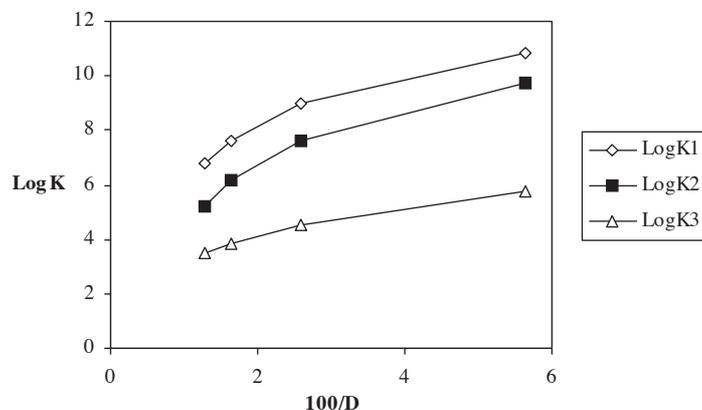


Figure 6. Variation in the stepwise stability constants of the iminodiacetic acid complexes of neodymium (III) with the inverse of the dielectric constant of the medium at 25 °C and I = 0.1.

Conclusions

In aqueous medium, and 20%, 45%, and 70% w/w dioxane-water mixtures only the mononuclear lanthanide (III) complexes of iminodiacetic acid with 1:1, 1:2, and 1:3 metal to ligand ratios formed.

The stability constants of the analogous complexes increased as the dioxane percentage increased (or as the dielectric constant of the medium decreased), as expected from the electrostatic nature of the interaction between the lanthanide ions and ligands.

The stability of all the analogous complexes, both in aqueous medium and in dioxane-water mixtures, were in the order of Nd(III) < Sm(III) < Gd(III) < Dy(III) < Er(III), as anticipated by the increasing charge density along the lanthanide series.

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