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Adsorption Equilibria of Copper(II) Ion on Octadecyl-Bonded Silica Gel in the Presence of β-Diketones

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Adsorptions of twelve β-diketones and their copper(II) complexes onto an octadecyl-bonded silica gel from an aqueous solution were measured by a batch technique. Several equilibrium constants for the adsorption reaction were measured and compared with those for solvent extraction. Using these constants, the abundance of each chemical species containing copper(II) ion in the presence of 2,4-pentanedione was calculated with respect to both the aqueous and the ODS gel phase.

Octadecyl-bonded silica (ODS) gel is very useful as a solid adsorbent for concentration of trace metals with chelating agents, and as a stationary phase of high-pressure liquid chromatography. Compared with solvent extraction, the concentration method has some advantages; simple procedure, free from a harmful solvent, and a large concentration ratio. However the adsorption behavior of metal ions in the presence of chelating agents is not fully understood. We reported the adsorption equilibria of copper(II) ion1) and various metal ions2) on ODS gel in the presence of 2,4-pentanedione. It was pointed out that many metal complexes with 2,4-pentanedione were adsorbed on the ODS gel as charged complexes in contrast to the solvent extraction in which the charge of an extractant must be neutral.

When the concentration of a metal ion by ODS gel is to be optimized, information about the substituent effect of the ligand is required. In general, if a higher concentration ratio is desired, a more hydrophobic ligand should be used. In this study we investigated the hydrophobic substituent effect of β-diketone on the ODS gel adsorption. The adsorption behavior was compared with data for solvent extraction. For solvent extraction, more data has been reported and accumulated,3) and the substituent effect on the extraction constants has also been studied.4,5) The adsorption parameters of twelve β-diketones, R–CO–CH$_2$–CO–R′ (R, R′=alkyl), and their copper(II) complexes were measured by a batch technique. Using these adsorption parameters, the abundance of each species containing copper(II) ion in the presence of 2,4-pentanedione were calculated as a function of pH.

Experimental

Reagents. 2,4-Pentanedione (Chromatographic reagent grade Kishida Kagaku) and 2,4-hexanedione (Guaranteed reagent grade, Kanto Kagaku) were used without further purification. Other β-diketones, 2,4-heptanedione, 2,4-octanedione, 2,4-decanedione, 3,5-heptanedione, 3,5-octanedione, 3,5-nonanedione, 3,5-undecanedione, 4-6-nonanedione, 4,6-decanedione, and 4,6-dodecanedione were prepared by the method proposed by Hauser and Adams.6) The synthesized β-diketones were purified by fractional distillation. Their chemical compositions were confirmed by ^{1}H NMR (CDCl$_3$, 270 MHz, Jeol JNM-GX270) and their purities were measured by gas chromatography (PEG-20 M as column packing reagent, Shimadzu GC-8A). The purities of 2,4-heptanedione, 2,4-octanedione, 2,4-decanedione, 3,5-heptanedione, 3,5-octanedione, 3,5-nonanedione, 3,5-undecanedione, 4,6-nonanedione, 4,6-decanedione, and 4,6-dodecanedione were 98, 97, 95, 98, 99, 99, 97, 99, 97, and 95%,respectively. The type of ODS gel method was C-18 75A purchased from GL Sciences, washed by the method described in a previous paper.1) All the reagents used were of guaranteed reagent grade.

Apparatus. pHs were measured by a Toyo Kagaku TD-4 pH meter. The copper(II) concentration in solutions and various β-diketones were measured by the same method as in our previous paper.1)

Procedure. The procedure for investigating adsorption equiliblia were the same as that described in our previous paper.1) The temperature during measurements was maintained at 298±1 K. Because of the low solubility of most of β-diketones in water except for 2,4-pentanedione and 2,4-hexanedione, they were used after they were adsorbed on the ODS gel in the following way: Two mmol of β-diketone was dissolved in 30 cm^3 of heptane, 10 g of ODS gel was dispersed into the heptane solution, and then this was dried under reduced pressure at room temperature. Total amounts of β-diketones and copper(II) ion were 1×10^{-4} mol and 3.14×10^{-7} mol, respectively, in the final mixture containing 20 cm^3 of aqueous solution and 0.5 g of the ODS gel. The ionic strength (μ=0.1) and pH of aqueous solution were adjusted by dilute solution of NaClO$_4$, HClO$_4$, or NaOH.

The adsorption equilibria and parameters of this system were treated in the same way as the distribution equilibria of liquid–liquid extraction reported previously.2)

The adsorption ratio, D_i, is defined as follows,

$$D_i(\mathrm{cm}^3\,\mathrm{g}^{-1}) = C_\mathrm{g}/C_\mathrm{a}, \qquad (1)$$

where C_g and C_a are concentrations of i species in gel and aqueous phase, respectively.

Results and Discussion

Adsorption Behavior of β-Diketones. The acid dissociation constants of twelve β-diketones were measured by the procedure reported by Koshimura and Okubo,4) which is a popular method for the measurement of acid dissociation constants by spectrophotometry. The pK_a values of them are listed in Table 1. The dissociation constants decrease with increments of carbon atoms of β-diketones.

Table 1. Acid Dissociation Constants of β-Diketones and Distribution Constants of the Acidic Type

	pK_a	$\log K_{d_{HA}}$
2,4-Pentanedione	9.0	1.3
2,4-Hexanedione	9.0	1.7
2,4-Heptanedione	9.0	2.0
2,4-Octanedione	9.2	2.3
2,4-Decanedione	9.2	3.2
3,5-Heptanedione	9.6	2.1
3,5-Octanedione	9.6	2.4
3,5-Nonanedione	9.7	2.8
3,5-Undecanedione	9.7	3.7
4,6-Nonanedione	9.6	2.8
4,6-Decanedione	9.6	3.2
4,6-Dodecanedione	9.6	3.8

The adsorption ratios of three 2,4-alkanediones, D_A, measured in the acidic region are shown in Fig. 1. The adsorption ratio of β-diketone is represented as follows,

$$D_A = ([HA]_g + [A^-]_g) \ / \ ([HA]_a + [A^-]_a), \qquad (2)$$

where $[HA]_g$ and $[A^-]_g$ are the concentrations of the acidic type and the basic type on the ODS gel, and $[HA]_a$ and $[A^-]_a$ are those in the solution, respectively. The distribution constants of the acidic type and the basic type, $K_{d_{HA}}$ and $K_{d_{A^-}}$ are defined as follows, respectively.

$$K_{d_{HA}} = [HA]_g/[HA]_a \text{ and } K_{d_{A^-}} = [A^-]_g/[A^-]_a. \qquad (3)$$

In acidic solution, since $[A^-]_a$ is so small as to be negligible in Eq. 2 (all β-diketones; $pK_a > 9$), the adsorption ratio is converted into the following equation,

$$D_A = K_{d_{HA}} + K_a K_{d_{A^-}} \ / \ [H^+]. \qquad (4)$$

Although in Eq. 4, D_A is a function of pH, the experimental data are apparently independent of pH. This means that the contribution of the second term of Eq. 4 is very small, that is, the adsorption ratio in the acidic region is almost equal to the distribution constant of acidic type of β-diketone.

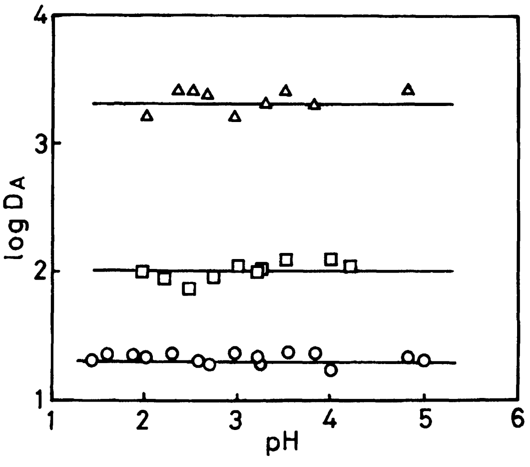

Fig. 1. Adsorption ratios of three 2,4-alkanediketones between ODS gel and acidic solution. (○) 2,4-pentanedione, (□) 2,4-heptanedione, (△) 2,4-decanedione.

The distribution constants of twelve β-diketones measured in this study are listed in Table 1. The correlation between $\log K_{d_{HA}}$ and number of carbon atoms of the β-diketones is shown in Fig. 2 along with the correlation obtained from the benzene–water extraction equilibrium.[5] There is a linear relationship with a slope of 0.38 ($\log K_{d_{HA}}$/carbon atoms), which is smaller than the value for the benzene–water extraction (slope: 0.61).[5] In most solvent extraction, the slope was in the range 0.60 to 0.64 for nonpolar solvents, and in the range 0.33 to 0.58 for polar solvents.[7]

Distribution constants are defined in terms of solubilities in water and organic solvents. The solubility of hydrocarbons and amphiphilic compounds in water and organic solvents has been recognized very perceptively by Tanford[8] as a hydrophobic effect. The standard free energy change for transfer of hydrocarbons from aqueous solution to pure liquid hydrocarbon increased linearly with the length of the hydrocarbon chain, and its slope is about 3.7 $\text{kJ mol}^{-1}/\text{CH}_2$ which almost equals the contribution to the free energy change of hydrocarbons and many amphiphilic compounds from nonpolar organic solvent to water. The value of the slope corresponds to $\Delta\log K_d/\text{CH}_2 = 0.65$ in the equilibrium constant. That is, the solubility of amphiphilic compounds in water depends upon the methylene group, but in nonpolar solvents the solubility is independent. However, in polar solvent extraction, the value of $\Delta\log K_d/\text{CH}_2$ is small, and the contribution of the methylene groups to the solubility is significant. It is considered that the

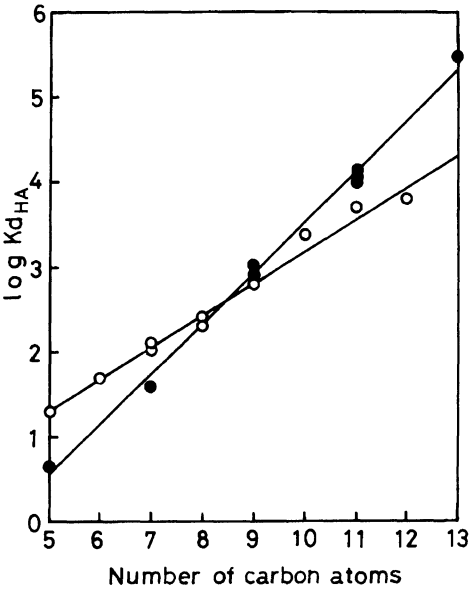

Fig. 2. Correlation between the adsorption constants of acid type β-diketones and methylene groups in their molecules. (○) ODS gel adsorption, (●) the distribution constants of benzene extraction from Ref. 5.

significant contribution of methylene groups to the solubility results from particular interaction between methylene group and solvent or insufficient dehydration of solute in a water-miscible polar orgnic solvent. Consequently, since the adsorption of β-diketones on the ODS gel is $\Delta\log K_d/CH_2=0.38$, they may still be hydrated partially on the surface between water and octadecyl groups.

Adsorption Behavior of Copper(II) Ion in the Presence of β-diketones. The adsorption behavior of copper(II) ion in the presence of three 2,4-alkanediketones on the ODS gel is shown in Fig. 3. In the absence of β-diketones, copper(II) ion was not adsorbed on the ODS gel below pH 5.5. Therefore the adsorbed copper(II) ion in the presence of β-diketones below pH 5.5 can be regarded as only copper(II)–diketone complexes. The curves are sigmoid like a typical curve obtained in solvent extraction. Similar curves were also obtained in the presence of the other nine diketones. Although adsorption of copper(II) started above pH 2 irrespective of the kind of β-diketone, the longer the chain length of ligands, the sharper the slope of the curves. Copper(II) ion was completely adsorbed above pH 5 in the presence of higher β-diketones.

Figure 4 shows the dependence of the adsorption ratio of copper(II) ion upon pH. In dilute copper(II) solutions, the adsorption ratio is as follows,

$$\log D_{\mathrm{Cu}} = \log K_{\mathrm{ad}} + n\log[\mathrm{HA}]_{\mathrm{g}} + n\mathrm{pH}, \qquad (5)$$

where K_{ad} is defined as the adsorption constant and n is the number of ligand molecules included in the adsorbed complex. Since the concentration of β-diketones added is in a large excess to the concentration of copper(II) ion, the concentration of β-diketones on the ODS gel, $[\mathrm{HA}]_{\mathrm{g}}$, can be regarded as a constant. The slope of $\log D_{\mathrm{Cu}}$ vs. pH represents the number of β-diketones in the adsorbed complexes. The adsorption constant is calculated from the intercept of the curves in Fig. 4. Two parameters of the twelve complexes measured are listed in Table 2.

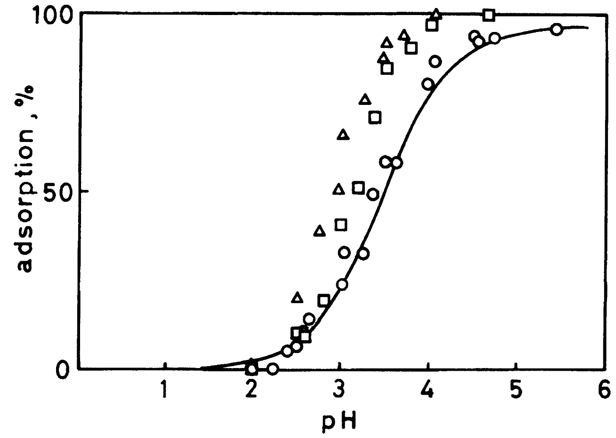

Fig. 3. pH dependence of adsorption of copper(II) ion onto the ODS get in the presence of 2,4-alkanediketone. (○) 2,4-pentanedione, (□) 2,4-heptanedione, (△) 2,4-decanedione. Solid line is calculated values of the adsorption of copper(II) in the presence of 2,4-pentanedione by use of six constants (K_a, $K_{d_{\mathrm{HA}}}$, β_1, β_2, $K_{d_{\mathrm{CuA}}}$, $K_{d_{\mathrm{CuA_2}}}$).

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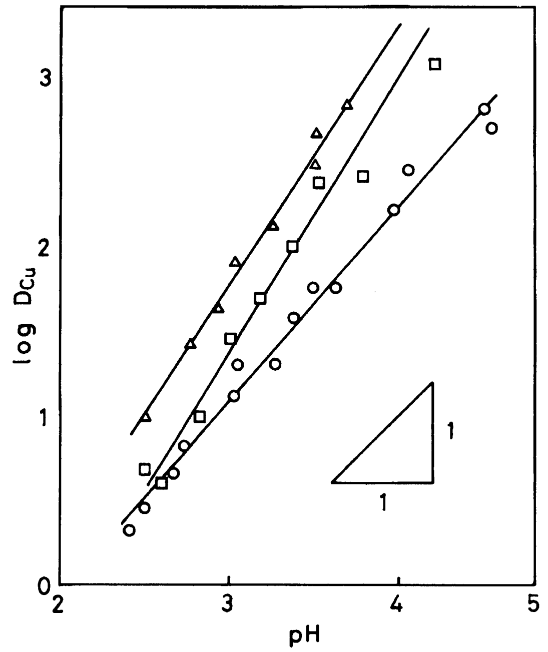

Fig. 4. Plot of $\log D_{\mathrm{Cu}}$ vs. pH in presence of 2,4-alkanediketone. (○) 2,4-pentanedione, (□) 2,4-heptanedione, (△) 2,4-decanedione.

The slopes for 2,4-pentanedione complex and 2,4-hexanedione complex are nearly unity and the others range between one and two, which indicates that 1 : 1 complexes are present on the ODS gel. In the benzene extraction all the slopes were two except for 2,4-pentanedione[5]. Since the copper(II) complexes are at the interface between the ODS gel and the aqueous solution, it is considered that the 1 : 1 complex with a charged site is stabilized at the interface like an ionic surfactant.

All adsorption constants, $\log K_{\mathrm{ad}}$, except 2,4-pentane-

Table 2. Number of Ligands and Adsorption Constants of β-Diketonate Complexes of Copper(II)

Ligand	n	$\log K_{\mathrm{ad}}$
2,4-Pentanedione	1.1	−1.0
2,4-Hexanedione	1.0	−1.0
2,4-Heptanedione	1.7	−2.2
2,4-Octanedione	1.6	−1.8
2,4-Decanedione	1.5	−1.8
3,5-Heptanedione	1.5	−2.0
3,5-Octanedione	1.8	−2.2
3,5-Nonanedione	1.9	−2.5
3,5-Undecanedione	1.7	−2.3
4,6-Nonanedione	1.6	−1.7
4,6-Decanedione	2.0	−2.4
4.6-Dodecanedione	1.6	−1.9

dione and 2,4-hexanedione are almost the same, about −2. The values of adsorption constants were larger than that for the extraction constants in benzene in which $\log K_{ex} = -4$.[5] The adsorption constant is represented as follows,

$$\log K_{ad} = \log \beta_n + \log K_{d_{CuA_n}} + n(\log K_a - \log K_{d_{HA}}), \quad (6)$$

where β_n and $K_{d_{CuA_n}}$ are the stability constants and the distribution of CuA_n complex. It is reported that the stability constants are linearly related to the dissociation constants of some β-diketones as follows:[9]

$$1/n \ \log \beta_n = -0.85 \ \log K_a + \text{const.} \quad (7)$$

Substituting Eq. 7 for β in Eq. 6 yields the following equation,

$$\log K_{d_{CuA_n}} = n \ \log K_{d_{HA}} + 0.15n \ \log K_a + \text{const.} \quad (8)$$

Since the variance of acid dissociation constants among twelve β-diketones is small, the distribution constant of each complex on the ODS gel is almost proportional to the nth power of the distribution constant of the ligand. Because of the linear relationship between $\log K_{d_{HA}}$ and the number of carbon atoms of β-diketone in Fig. 2, it is expected that $\log K_{d_{CuA_n}}$ increases by a factor of about $0.38n$ with increments of the number of the carbon atoms.

Abundance of Chemical Species of Copper(II) Ion in Presence of 2,4-Pentanedione in Water–ODS Gel System. Most of the stability constants of copper(II)–β-diketone complexes have not been measured except for the 2,4-pentanedione complex. If each distribution constant of the CuA^+ and the CuA_2 complexes with 2,4-pentanedione can be calculated, the adsorption equilibria are understood more clearly.

When the chemical species of copper(II) ion on the ODS gel is present as CuA^+ and CuA_2, the adsorption ratio observed can be described as follows,

$$D_{Cu} = \frac{[CuA^+]_g + [CuA_2]_g}{[Cu^{2+}]_a + [CuA^+]_a + [CuA_2]_a}, \quad (9)$$

where the brackets with subscript g indicate the concentration in the ODS gel, in mol kg^{-1}, and the brackets with a indicate the concentration in aqueous solution, in mol dm^{-3}. Equation 9 is transformed using the equilibrium constants in water and on the ODS gel as follows,

$$D_{Cu} = \frac{K_{d_{CuA}} K_1/[H^+] + K_{d_{CuA_2}} K_2/[H^+]^2}{1 + K_1/[H^+] + K_2/[H^+]^2}, \quad (10)$$

where

$$K_1 = (\beta_1 K_a/K_{d_{HA}})[HA]_g, \ K_2 = (\beta_2 K_a^2/K_{d_{HA}}^2)[HA]_g^2. \quad (11)$$

$K_{d_{CuA}}$ and $K_{d_{CuA_2}}$ are distribution constants of CuA^+ and CuA_2, respectively. Because a large excess of β-diketone to copper(II) ion is present on the ODS gel, the concentration of the ligand on the ODS gel, $[HA]_g$, is considered to be constant. Consequently, Eq. 10 is converted into the following equation.

$$D_{Cu}([H^+] + K_1 + K_2/[H^+]) = K_{d_{CuA}} K_1 + K_{d_{CuA_2}} K_2/[H^+]. \quad (12)$$

The relationships between $D_{Cu}([H^+]+K_1+K_2/[H^+])$ vs. $1/[H^+]$ is shown in Fig. 5. Although the deviation of data at the high pH region is considerable, the $K_{d_{CuA}}$ and $K_{d_{CuA_2}}$ can be calculated from the slope and the intercept by the linear least square method. Using the stability constants obtained from the literature,[10] $\log \beta_1 = 8.16$ and $\log \beta_2 = 14.76$, the values of $\log K_{d_{CuA}}$ and $\log K_{d_{CuA_2}}$ were found to 1.3 and 3.1, respectively.

In the solvent extraction of copper ion with 2,4-pentanedione, the slope based on Eq. 5 was nearly unity.[5,11] Sekine and Ihara[11] reported that the deviation from $n = 2$ could be analyzed by an assumption of only non-charged complex for the extraction species. However in the ODS gel adsorption system, Fig. 5 indicated that the intercept is not zero and the term of $K_{d_{CuA}} K_1$ is significant. It is confirmed that charged 1 : 1 complex is also present on the ODS gel as reported previously.[1,12]

The abundance of the species containing copper(II) ion in the presence of 2,4-pentanedione are shown in Fig. 6. Figure 6 was calculated from six constants (K_a, $K_{d_{HA}}$, β_1, β_2, $K_{d_{CuA}}$, $K_{d_{CuA_2}}$) and the total concentrations of copper(II) ion and 2,4-pentanedione. The solid line in Fig. 3 was drawn with the sum of $[CuA^+]_g$ and $[CuA_2]_g$ in Fig. 6. The line agrees with the observed values as shown in Fig. 3.

Conclusion

Adsorption parameters of twelve β-diketones and their copper(II) complexes on the ODS gel were obtained. It was found that the contribution of the hydro-

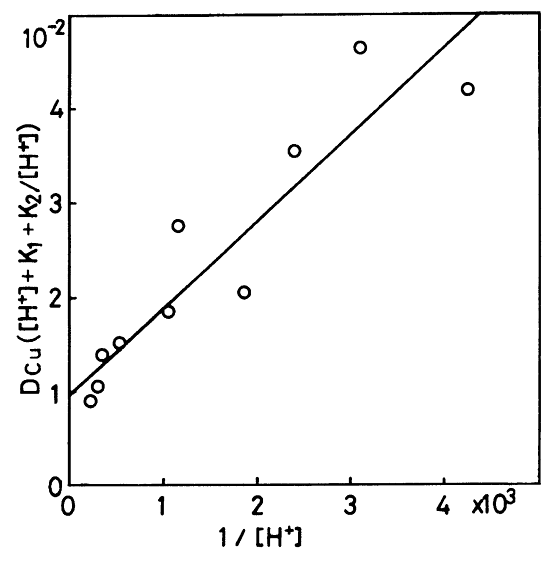

Fig. 5. Plot of D_{Cu} $([H^+]+K_1+K_2/[H^+])$ vs. $1/[H^+]$.

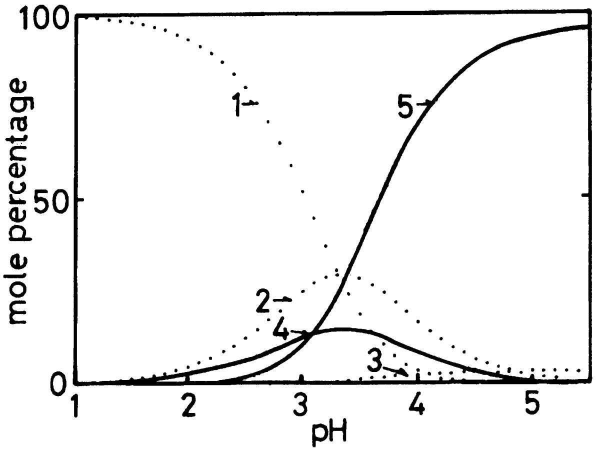

Fig. 6. Mole percentage of five species containing copper(II) ion. Dashed lines; 1 Cu^{2+}, 2 CuA^+, and 3 CuA_2, in solution. Solid lines; 4 CuA^+ and 5 CuA_2, on the ODS gel.

phobic substituent effect to the ODS gel adsorption was smaller than that of the solvent extraction with nonpolar organic solvent. The logarithm of the distribution constant of acid type β-diketone, $\log K_{d_{HA}}$, increased by a factor of 0.38 with increment of its carbon number. Also that of the copper(II) β-diketonate complex, $\log K_{d_{CuA_n}}$, increased by a factor of $0.38n$ (n: number of ligands in complex) with each increment of the number of the carbon atoms. On the basis of these results, a detailed figure of the adsorption of copper(II) ion in presence of 2,4-pentanedione could be illustrated by use of the adsorption parameters obtained.

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