Studies on the Extraction of Metal Complexes

XVI. Distribution Studies on the Complex Formation of U(VI) with Salicylic Acid and Methoxybenzoic Acid

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The complex formation of UO_2^{2+} and salicylic acid, H_2A , has been studied by means of distribution data. The solvent system was hexone — 0.1 M NaClO_4 and the temperature 25°C . The UO_2^{2+} concentration was varied between 10^{-3} M and 5×10^{-5} M, while the salicylic acid concentration was varied between 1 M and 10^{-2} M. The results indicate that the predominant species in the hexone phase are (for the representation of the complexes, cf. Ref.⁹) $\text{UO}_2(\text{H}_2\text{A})_2(\text{H}^+)_2$ and $\text{UO}_2(\text{H}_2\text{A})_3(\text{H}^+)_3$. Complexes formed in appreciable amounts in the aqueous phase in the pH-range 3–5 seem to be $\text{UO}_2(\text{H}_2\text{A})(\text{H}^+)_1$ and $\text{UO}_2(\text{H}_2\text{A})(\text{H}^+)_2$. The equilibrium constants for the formation of these complexes are given in Table 1. Comparative experiments were run with methoxybenzoic acid (HB). The extractable complex is UO_2B_2 . In the aqueous phase $\text{UO}_2(\text{B})(\text{OH})$ seem to form. The equilibrium constants for the methoxy-complexes are given in Table 2.

Although salicylic acid, H_2A , is known to form complexes with U(VI) and use of this tendency has been made in analytical chemistry¹, no quantitative information can be found regarding how the complexes are built up or about their stability.

Salicylic acid is a dibasic acid. The first dissociation constant $k'_a = 10^{-2.82}$ and the distribution constant $k_d = 10^{2.51}$ of the acid between hexone and water have been determined previously². The second dissociation constant k''_a due to the phenolic hydrogen, is approximately^{3,15} 10^{-13} . In acidic and neutral solutions only undissociated acid, H_2A , and the ion HA^- will be present. However, there are reports in the literature that salicylic acid very often forms chelate compounds with metals^{4,5}. The following reaction is therefore conceivable

The ligand may thus be either HA^- or A^- . The ability to form a chelate compound by removal of the phenolic hydrogen is lost with methoxybenzoic acid

as the ligand. Since the ligands are very similar, a comparison of these two reagents was made in order to see whether the data indicated that a displacement of the phenolic hydrogen during complex formation took place.

In the present paper extraction data for the system U(VI)-salicylic acid-H₂O-hexone are presented. The data are analysed in order to find which complexes are formed in appreciable amounts and possible equilibrium constants for the formation of these complexes are calculated. Data are also presented for the system U(VI)-methoxybenzoic acid-H₂O-hexone so that comparison of the two ligands can be made.

EXPERIMENTAL

Chemicals. A standard solution of UO₂(ClO₄)₂ in 0.1 M HClO₄ was prepared by dissolving UO₂ of a very pure quality in a known excess of acid. The concentration of the solution was determined by evaporation of an aliquot and ignition to U₃O₈. Salicylic acid of analytical grade was used without further purification. The hexone used was of technical grade. After filtration it was washed with HClO₄ and NaOH in order to remove any basic and acidic impurities and thereafter several times with water.

Procedure. All experiments were carried out at 25°C and the ionic strength was adjusted to 0.1 M with NaClO₄. In the experiments a solution of salicylic acid in hexone was shaken for at least 18 hours with an equal volume of an aqueous UO₂²⁺ solution. After equilibration, the two phases were centrifuged and separated. The hydrogen ion concentration of the aqueous phase was measured with a Radiometer valve potentiometer, type 3i. The uranium analyses were made by a fluorimetric method⁶ (the fluorimeter used was constructed at AB Atomenergi). Only the phase containing the smaller fraction uranium was analysed. The uranium content of the other phase was obtained by difference from the total uranium content. Tests for material balance were only made in a few cases since no precipitate was ever noticed in the solutions. Aliquots of the sample liquid were taken out for analyses and evaporated on a platinum disc. Hexone solutions with high salicylic acid concentration were extremely difficult to evaporate without loss. Furthermore, there was a risk that too large a residue would catch fire in the fusion procedure. 90 % NaF and 10 % Na₂CO₃ was used as mixed flux. Blank determinations were run at the same time and subtracted. A calibration curve was obtained from known UO₂(ClO₄)₂-solutions.

The colorimetric determination of uranium by the oxine-extraction method⁷ gave no reliable results because of too high blank readings of the salicylic acid.

The experiments were started with constant initial concentration of salicylic acid in the organic phase [H₂A]_{tot}. In all experiments [H₂A]_{tot} >> [U]_{tot} so that the addition of [U]_{tot} does not change the ligand concentration in the solution. The calculation of the concentrations [HA⁻] and [H₂A]_{aq} at different pH was made according to eqns. (2) and (3) for equal phase volumes

$$[\text{HA}^-] = \frac{k_a [\text{H}_2\text{A}]_{\text{tot}}}{[\text{H}^+] (k_a + 1 + k_a/[\text{H}^+])} \quad (2)$$

$$[\text{H}_2\text{A}]_{\text{aq}} = \frac{[\text{H}_2\text{A}]_{\text{tot}}}{(k_a + 1 + k_a/[\text{H}^+])} \quad (3)$$

Since k_a is large, the denominator in eqn. (3) is unaffected of the ratio $k_a/[\text{H}^+]$ for $[\text{H}^+] > k_a$; thus $[\text{H}_2\text{A}]_{\text{aq}}$ remains constant in the aqueous phase up to pH ~ 3 after which it starts to decrease with increasing pH.

RESULTS

The U(VI)-salicylic acid system

For mononuclear complex reactions q , the distribution ratio of the metal, must be independent of the metal concentration. For this purpose the initial uranium concentration was varied between 10^{-3} M and 5×10^{-5} M. In Fig. 1 the logarithm of the distribution ratio q is plotted against $-\log[H^+]$ for different initial salicylic acid concentrations. The curves show no systematic spread for uranium concentrations $\leq 2.5 \times 10^{-4}$ M. It may therefore be concluded that the presence of polynuclear complexes can be neglected in solutions of U(VI) and salicylic acid when $[U]_{\text{tot}} \leq 2.5 \times 10^{-4}$ M.

For $[U]_{\text{tot}} = 10^{-3}$ M the points fall on the curves of the lower uranium concentrations up to a pH about 3 (Fig. 1). However, for $[H_2A]_{\text{tot}} = 0.1$ M, the

Fig. 1. Variation of the distribution ratio q of U(VI) with $-\log [H^+]$ for different initial salicylic acid concentrations, $[H_2A]_{\text{tot}}$. The full lines enclosing the shaded area represent the estimated limits of error, when curves are calculated according to eqn. (15).

Fig. 2. Variation of the distribution ratio q of $U(VI)$ with $-\log [HA^-]$ for different initial salicylic acid concentrations, $[H_2A]_{tot}$.

Fig. 3. Variation of the distribution ratio q of $U(VI)$ with $-\log [H^+]$ for different initial methoxybenzoic acid concentrations, $[HB]_{tot}$.

lowest reagent concentration tested with $[U]_{tot} = 10^{-3}$ M, a marked decrease of the values of q was noticed for $pH > 3.5$ indicating polynuclear complexes. These data have not been recorded in Fig. 1 for the sake of clarity ($\Delta \log q > 0.3$).

The $U(VI)$ -methoxybenzoic acid system

The investigation was carried out for $[U]_{tot} = 10^{-4}$ M since this concentration could be expected from the experiments with salicylic acid to involve chiefly mononuclear reactions. Because of the lower solubility of methoxybenzoic acid in hexone the highest reagent concentration that was tested was 0.3 M (saturated solutions in hexone ~ 0.7 M). In order to calculate the anion concentration the ratio k_a/k_d was determined by a two phase titration. Two different titrations gave an average value of $k_a/k_d = 10^{-5.43 \pm 0.01}$. For the same ionic strength (0.1 M) a value of $k_a = 10^{-3.89 \pm 0.01}$ is derived from values reported in the literature⁸, whence $k_d = 10^{1.54 \pm 0.02}$. If HB refers to undissociated methoxybenzoic acid, $[B^-]$ is calculated according eqn. (2). The data are represented in Figs. 3—4.

Calculation of the formation constants

In all experiments the uranium concentration was kept smaller than the ligand concentration by a factor of 10^2 or more. The change in ligand concentration due to formation of uranium complexes can therefore be disregarded. Furthermore, only uncharged complexes are believed to dissolve in the organic phase.

Fig. 4. Variation of the distribution ratio q with $-\log [B^-]$ for different initial methoxybenzoic acid concentrations, $[HB]_{\text{tot}}$.

In Fig. 2 the graphical representation of $\log q$ versus $-\log [HA^-]$ is given. If q were a function of $[HA^-]$ only all the curves would coincide for varying $[H_2A]_{\text{tot}}$ and the data could be explained by the standard approach that the simplest uncharged complex, in this case $UO_2(HA)_2$, dissolves in the organic phase. However, q is observed to increase with increasing $[H_2A]_{\text{tot}}$, which indicates that the complex in the organic phase must have H_2A -molecules associated with it.

Let the general formula $UO_2(H_2A)_x(H^+)_{-y}$ describe the complexes present⁹. The complexity product of these complexes is denoted by K_{xy} and the distribution coefficient of the uncharged complexes by A_{x2} . The general equation of the distribution ratio q then takes the following form (cf. Ref.⁹)

$$q = \frac{\sum A_{x2} K_{x2} [H_2A]^x [H^+]^{-2}}{1 + [H^+]^{-1} \sum K_{x1} [H_2A]^x + [H^+]^{-2} \sum K_{x2} [H_2A]^x + [H^+]^{-3} \sum K_{x3} [H_2A]^x + \dots} \quad (4)$$

As a reasonable assumption the pure hydroxo complex $UO_2(OH)_2$ was not considered to dissolve in the organic phase, which means that $x > 1$ in the numerator in eqn. (4). Furthermore, from the slope of plots of $\log q [H^+]^2$ against $\log [H_2A]_{\text{aq}}$ for various pH's it was confirmed that x must be > 2 . In Fig. 5 $\log q [H^+]^2 [H_2A]^{-2}$ is plotted against $\log [H_2A]_{\text{aq}}$ for varying pH; values of q were taken from the smooth curves drawn through the experimental points in Fig. 1 at pH 1.0, 1.6, 2.0, etc. With decreasing pH the curves coincide to one curve indicating that $q [H^+]^2 [H_2A]^{-2}$ is independent of the hydrogen ion concentration and approaches the following expression (cf. eqn. (4))

$$q [H^+]^2 [H_2A]^{-2} = A_{22} K_{22} + A_{32} K_{32} [H_2A] + A_{42} K_{42} [H_2A]^2 + \dots \quad (5)$$

Fig. 5. The calculation of the coefficients $A_{22}K_{22}$ according to eqn. (5).

The unknown constants $A_{22}K_{22}$ in eqn. (5) can be determined by a graphical procedure recommended by Sillén¹⁰. The curve for pH 1.0—2.6 in Fig. 5 was first compared with a plot $\log y (\log x)$ where $y = 1 + x$ to test whether $A_{42}K_{42} = 0$. Since a good agreement was obtained when the two curves were fitted with each other it was concluded that $A_{42}K_{42} = 0$ in eqn. (5) and that the polynomial was of the first order. The unknown coefficients $A_{22}K_{22}$ and $A_{32}K_{32}$ are obtained from the points of intersection of the asymptotes (dotted lines in Fig. 5)

$$\log A_{22}K_{22} = 0.92 \pm 0.02 \quad (6)$$

$$\log \frac{A_{32}K_{32}}{A_{22}K_{22}} = 2.56 \pm 0.05 \quad (7)$$

$$\therefore \log A_{32}K_{32} = 3.48 \pm 0.07 \quad (8)$$

For pH > 3 the curves in Fig. 5 are no longer independent of the hydrogen ion concentration. The data show that the UO_2^{2+} ions here form complexes in the aqueous phase. In order to find which complexes the following function was set up

$$\varphi = q^{-1} [\text{H}_2\text{A}]^2 [\text{H}^+]^{-2} (10^{0.92} + 10^{3.48} [\text{H}_2\text{A}]) \quad (9)$$

Suppose that a stepwise formation of the complexes $\text{UO}_2(\text{HA})^+$ and $\text{UO}_2(\text{HA})_2$ takes place in the aqueous phase, then φ would be a function of $[\text{H}_2\text{A}][\text{H}^+]^{-1}$ only. Fig. 6 shows that this is not so; φ has been calculated for experimental points obtained with $[\text{U}]_{\text{tot}} = 10^{-4}$ M. The function ψ defined by eqn. (10) was calculated next

$$\psi = (\varphi - 1) [\text{H}_2\text{A}]^{-1} [\text{H}^+] \quad (10)$$

Fig. 6. Variation of $\log \phi$ with $\log [H_2A][H^+]^{-1}$. ϕ is calculated according to eqn. (9) for experimental points obtained with $[U]_{\text{tot}} = 10^{-4} M$.

In Fig. 7 $\log \psi$ has been plotted against $-\log [H^+]$. Now, according to eqn. (4) the function ψ is when developed for $x > 1$.

$$\psi = K_{11} + K_{12} [H^+]^{-1} + \dots [H_2A] (K_{21} + K_{22} [H^+]^{-1} + \dots) + [H_2A]^2 (K_{31} + K_{32} [H^+]^{-1} + K_{33} [H^+]^{-2} + \dots) + \dots \quad (11)$$

From Fig. 7 it is seen that $\log \psi$ increases with $-\log [H^+]$. On the other hand, for a value of $-\log [H^+]$ that is fixed, $\log \psi$ appears to decrease if anything with increased $[H_2A]_{\text{tot}}$ or $[H_2A]$. This decrease of ψ cannot be real since K_{xy} must be positive because of the law of mass action. It was therefore concluded that the experimental data spread around the curve: $\psi = K_{11} + K_{12} [H^+]^{-1}$. From the point of intersection of the asymptotes (dotted lines in Fig. 7) the coefficients K_{11} and K_{12} were estimated

$$\psi = 10^{-0.62 \pm 0.05} + 10^{-4.5 \pm 0.2} [H^+]^{-1} \quad (12)$$

The complexes that seem to form in the aqueous phase are therefore according to eqns. (10) and (11)

$$[U]_{\text{tot aq}} = [UO_2^{2+}] + [UO_2(H_2A)(H^+)_{-1}] + [UO_2(H_2A)(H^+)_{-2}] \quad (13)$$

The complexes present in the organic phase are (cf. eqns. (6) and (8) with (5))

$$[U]_{\text{tot org}} = [UO_2(H_2A)_2(H^+)_{-2}] + [UO_2(H_2A)_3(H^+)_{-2}] \quad (14)$$

The equilibrium constants are summarized in Table 1. With these sets of constants the equation of the distribution ratio follows eqn. (15)

$$q = \frac{[H_2A]^2 [H^+]^{-2} (10^{0.92 \pm 0.02} + 10^{3.48 \pm 0.07} [H_2A])}{1 + 10^{-0.62 \pm 0.05} [H_2A][H^+]^{-1} + 10^{-4.5 \pm 0.2} [H_2A][H^+]^{-2}} \quad (15)$$

Fig. 7. The calculations of K_{11} and K_{12} (cf. eqn. (11)). Abscissa: $-\log [H^+]$. Ordinate = $\log \psi$, which is calculated according to eqn. (10) for experimental points obtained with $[U]_{\text{tot}} = 10^{-4} M$. The broken lines enclosing the shaded area represent the estimated limits of error for a curve following eqn. (12).

In Fig. 1 the shaded area represents eqn. (15) with the above uncertainty estimated for the constants. In Fig. 8 the percentage of the different U(VI) complexes in the aqueous phase is plotted as functions of the salicylate concentration, and the hydrogen ion concentration.

Although methoxybenzoic acid was studied in less detail and therefore less reliance can be put on the constants derived, the same treatment of the data was made. In the case of methoxybenzoic acid the only complex extracted

Fig. 8. The fraction of different U(VI) complexes in the aqueous phase. Abscissa: $-\log [HA^-]$ or $-\log [H^+]$. Ordinate: the percentage of a certain complex (the vertical distance of the curve above the zero line represents the percentage).

into the organic phase seems to be $\text{UO}_2(\text{HB})_2(\text{H}^+)_{-2}$ or $\text{UO}_2(\text{B})_2$. The experimental data can be approximated assuming only the complex $\text{UO}_2(\text{HB})(\text{H}^+)_{-2}$ or $\text{UO}_2(\text{B})(\text{OH})$ in the aqueous phase. With this assumption the equation for q takes the following form

$$q = \frac{10^{-1.56 \pm 0.05} [\text{HB}]^2 [\text{H}^+]^{-2}}{1 + 10^{-5.85 \pm 0.10} [\text{HB}][\text{H}^+]^{-2}} \quad (16)$$

The full curves in Fig. 3 are calculated according to eqn. (16). Estimated values of the equilibrium constants are given in Table 2.

Table 1. Equilibrium constants derived for U(VI) from distribution data with salicylic acid, H_2A , in the system hexone — 0.1 M NaClO_4 .

$$\begin{aligned} A_{22}K_{22} &= 10^{0.92 \pm 0.02} \quad \frac{[\text{UO}_2(\text{H}_2\text{A})_2(\text{H}^+)_{-2}]_{\text{org}}}{[\text{UO}_2(\text{H}_2\text{A})_2(\text{H}^+)_{-2}]_{\text{org}}[\text{H}_2\text{A}]_{\text{org}}} = 10^{0.95 \pm 0.12} \\ A_{32}K_{32} &= 10^{3.48 \pm 0.07} \\ K_{11} &= \frac{[\text{UO}_2(\text{H}_2\text{A})(\text{H}^+)_{-1}]}{[\text{UO}_2^{2+}][\text{H}_2\text{A}][\text{H}^+]^{-1}} = 10^{-0.62 \pm 0.05} \quad \frac{[\text{UO}_2(\text{HA})^+]}{[\text{UO}_2^{2+}][\text{HA}^-]} = 10^{2.2} \\ K_{12} &= \frac{[\text{UO}_2(\text{H}_2\text{A})(\text{H}^+)_{-2}]}{[\text{UO}_2^{2+}][\text{H}_2\text{A}][\text{H}^+]^{-2}} = 10^{-4.5 \pm 0.2} \quad \frac{[\text{UO}_2(\text{HA})(\text{OH})]}{[\text{UO}_2^{2+}][\text{HA}^-][\text{OH}^-]} = 10^{12.1} \end{aligned}$$

Table 2. Equilibrium constants derived for U(VI) from distribution data with methoxybenzoic acid, HB , in the system hexone — 0.1 M NaClO_4 .

$$\begin{aligned} A_{22}K_{22} &= 10^{-1.56 \pm 0.05} \\ K_{12} &= \frac{[\text{UO}_2(\text{HB})(\text{H}^+)_{-1}]}{[\text{UO}_2^{2+}][\text{HB}][\text{H}^+]^{-1}} = 10^{-5.85 \pm 0.10} \quad \frac{[\text{UO}_2(\text{B})(\text{OH})]}{[\text{UO}_2^{2+}][\text{B}^-][\text{OH}^-]} = 10^{11.9} \end{aligned}$$

DISCUSSION

Formula of the complexes. In the previous section the salicylate complexes have been described by the general formula $\text{UO}_2(\text{H}_2\text{A})_x(\text{H}^+)_{-y}$ and x and y were determined for the predominant species in the two phases (eqns. (13) and (14)). As was mentioned in the beginning of the present paper the structure of the salicylate complexes can be imagined as nonchelates (the ligand = HA^-) or as chelate compounds (the ligand = $\text{A}^{=}$). Since the complexes ($x = 2$, $y = 2$) and ($x = 3$, $y = 2$) are found in the organic phase, the following isomeric formulae are possible

In the aqueous phase complexes corresponding to ($x = 1$, $y = 1$) and ($x = 1$, $y = 2$) are shown to form. The former complex ($x = 1$, $y = 1$) is not compatible with $\text{A}^{=}$ as the ligand. The complexes possible in the aqueous phase are therefore $\text{UO}_2(\text{HA})^+$ and $\text{UO}_2(\text{HA})(\text{OH})$ or UO_2A . To distinguish between the above formulae is not possible. However, the close resemblance of the distribution curve found with methoxybenzoic acid suggests that the salicylate complexes are built up by HA^- ligands. Only two methoxybenzoic acid mole-

cules is found in the extracted uranyl complex. The fact that an additional acid molecule is not found with methoxybenzoic acid may be ascribed to the more limited space around the central group due to the $-\text{CH}_3$ (cf. the results obtained with Th¹¹).

Comparison with earlier work. Weinland and Hager¹² have reported compounds with two and three molecules of salicylic acid attached to the uranium. These compounds were formed in presence of alkali and organic bases and the authors proposed a structure where the uranyl group entered in the anion, as in $\text{C}_5\text{H}_5\text{N} \cdot \text{H}[\text{UO}_2(\text{HA})_3]$ with three salicylic acid molecules. Migration experiments with uranyl salicylate¹³ gave to result that the main part of the uranium migrated towards the cathode even at high concentrations of HA^- . It seems therefore more plausible to assign the following structure to the above complex: $\text{C}_5\text{H}_5\text{N} \cdot [\text{UO}_2(\text{HA})_2 \cdot \text{H}_2\text{A}]$.

Foley and Anderson¹⁴ have studied the complex formation between uranyl and sulfosalicylic acid (H_3R) spectrophotometrically. Some of the measurements were made in acetate buffers, which might invalidate the investigation. The ratio of uranyl to sulfosalicylate was found to be 1:1 in a pH range up to 6.1. The same ratio 1:1 of uranyl to salicylic acid is found by us in the aqueous phase in the present study. Further, the uranyl sulfosalicylate complex shows maximum absorption at a pH ~ 4.7 . Since the second dissociation constant^{14,15} of sulfosalicylic acid is about $10^{-2.7}$ the main part of the acid will be in the form HR^- at pH = 4.7. The decrease of absorption above pH 4.7 is explained as due to hydrolysis effects. No extraction into benzene or carbon

tetrachloride was found. An apparent equilibrium constant $K = \frac{[\text{UO}_2^{2+}][\text{R}]}{[\text{UO}_2\text{R}]}$, where $[\text{R}]$ stands for sulfosalicylic acid in all forms, was calculated to be 1.9×10^{-4} (25°C).

In Table 1 the equilibrium constant for the formation of $\text{UO}_2(\text{HA})^+$ is given, i. e. $10^{2.2}$. This value may be compared with the equilibrium constant for the first uranyl acetate complex, which has been determined by Ahrlund¹⁶ to $10^{2.6}$.

The hydrolysis of UO_2^{2+} . The data of the present investigation have been treated as if only mononuclear complex formation took place. Now the hydrolysis of the ion UO_2^{2+} has been investigated and discussed as a polymeric process¹⁷. To find out whether the experiments in the present study were carried out in a concentration range of polynuclear hydrolysis, a value of the function X is needed

$$X = \log [\text{U}]_{\text{tot aq}} - 2 \log [\text{H}^+] \quad (16)$$

By comparison with Ahrlund's diagram (cf. Ref.¹⁷, Fig. 1 or Fig. 5) one sees that for $X < 5$ no appreciable amounts of hydrolysis complexes are formed. Let us calculate a value of X for the lowest H_2A concentration used, i. e. $[\text{H}_2\text{A}]_{\text{tot}} = 10^{-2}$ M. A value of $[\text{U}]_{\text{tot aq}}$ is estimated from the distribution curves in Fig. 1, since $[\text{U}]_{\text{tot aq}} = [\text{U}]_{\text{tot}}/(q + 1)$. Thus at pH = 5 one obtains a value of $X = 5.4$, which suggests that these distribution experiments might be affected by the hydrolysis of the ion UO_2^{2+} . For H_2A concentrations $> 10^{-2}$ M and $[\text{U}]_{\text{tot}} = 10^{-4}$ M there is no danger of hydrolysis effects. For $[\text{U}]_{\text{tot}} =$

10^{-3} M and $[\text{H}_2\text{A}]_{\text{tot}} = 10^{-1}$ M the distribution curve was found to deviate from those obtained with lower $[\text{U}]_{\text{tot}}$, when pH increased above 3.5. The lower values of q that was obtained, indicate that water soluble polymeric complexes are formed. In this case the value of X is around 5.6.

Polymeric hydroxo complexes have been reported in the reactions of uranyl and organic acids (H_2R) such as citric acid, maleic acid and tartaric acid¹⁸. The uranium concentration and the concentration of the organic reagent were both 0.05 M. Dimers of the complexes UR held together by oxygen bridges were believed to be formed when the pH was raised to 3.5.

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