Separation of palladium(II) from mixtures of non-ferrous metal ions by solvent extraction

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The possibility of Pd(II) ions separation from mixtures of Co(II), Ni(II), Cu(II) and Pd(II) ions by solvent extraction was studied, using 1-hexyl-2-methylimidazole in chloroform as the extractant. The initial concentration of each ion was 10 mM. The tests were carried out at a temperature of 25°C, at a constant strength of the aqueous solution of I = 0.5, as maintained by the KCl solution.

It was demonstrated that differences in the stability and structure of their coordination sphere as well as solubility of complexes with the extractant could be used for separating the Co(II), Ni(II), Cu(II) and Pd(II) ions by solvent extraction. Pd(II), which forms flat-square complexes in the solutions, passes easily into the organic phase and is easier separated from the mixture of Co(II), Ni(II), Cu(II) ions, which form octahedral or tetrahedral complexes. Extraction percentages were calculated. For the respective metals, their values increase for increasing concentrations of the extractant in the aqueous phase. The extraction percentage decreases in the following order: Pd(II) > Cu(II) > Co(II) > Ni(II). In the case of the quaternary mixture, the highest extraction percentage for Pd(II) (70%) was obtained at a pH=7.33. Separation coefficients were also calculated. The highest separation coefficients were obtained for the system: Pd(II)/Ni(II), Pd(II)/Co(II); at a pH of 5.4 for an aqueous solution, their values are 13.3 and 7.7, respectively.

Keywords: metal separation, cobalt(II), nickel(II), copper(II), palladium(II), solvent extraction, alkylimidazole

Introduction

Commercial and bench-scale separation of non-ferrous metal ions from aqueous solutions may be effected by any of a number of techniques, including solvent extraction (liquid-liquid extraction), ion exchange, ion flotation, and sorption on polymer resins. The right choice depends on the concentration range of the components in the solution and on the properties of the compounds to be separated [1-3].

Platinum and palladium are very often found in sulfide ores of nickel and copper [4-6]. Their pyrometallurgic processing provides a Ni-Cu-Fe alloy, containing mostly platinum metals, which are separated from the base compounds by hydrometallurgic methods [7].

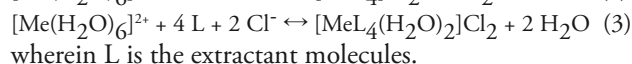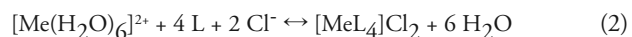Liquid-liquid solvent extraction is one of the most dynamically growing hydrometallurgic processes.

Optimization of extraction methods for the separation of metals calls for new, specific extractants, which are characterized by desirable properties, such as selectivity, easily conducted processes of extraction and re-extraction, low solubility in the aqueous phase, and low cost of the synthesis process. The suitable extractants are, for instance: carboxylic acids [8], derivatives of acid amides [9,10], amines [11,12], complex oximes [13,14], crown ethers [15,16], ketone derivatives [17], pyridine derivatives [18-20]. Derivatives of imidazole, including alkyl derivative, were used as extractants of transition metals [21-23] and carriers for metal cations in polymer inclusion membranes [24-27].

In aqueous solutions, cations of Co(II), Ni(II) and Cu(II) exist in the form of octahedral aquacomplexes $[M(H_2O)_6]^{2+}$. Owing to the effect of ligands (extractants), octahedral aquacomplexes of certain cations tend to change their coordination number (c.n.) from 6 to 4 and they change their coordination sphere into flat or tetrahedral, depending on the structure of their d-electron layer. The process is illustrated by the equation:

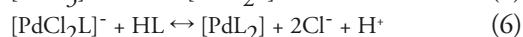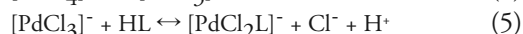$$[M(H_2O)_6]^{2+} \leftrightarrow [M(H_2O)_4]^{2+} + 2\ H_2O \qquad (1)$$
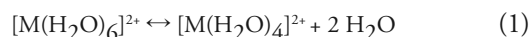
Therefore, tetrahedral or flat-square complexes (c.n.=4) are formed in the solution in addition to octahedral ones (c.n.=6). Tetrahedral complexes are specific to Co(II), whereas flat complexes may be formed by Ni(II). Also Cu(II) ions tend to change the symmetry of their coordination sphere, forming distorted tetrahedral or flat structures, square pyramids, or trigonal pyramids. Changes in the coordination sphere lead to higher sums of complex stability constants (stability constants are the sum of the stability constants for the complexes with c.n.=4 and with c.n.=6) and higher susceptibility to extraction in the liquid-liquid system, because complexes with the c.n.=4, being less hydrated, pass more readily into the organic phase after at least part of the molecules of water, which is bound in the metal coordination sphere, is replaced by the molecules of the more hydrophobic ligand. In the case of chloride solutions, this can be illustrated by the following equations for the fourth stage of complexation (n=4):

$$[Me(H_2O)_6]^{2+} + 4\ L + 2\ Cl^- \leftrightarrow [MeL_4]Cl_2 + 6\ H_2O \qquad (2)$$
$$[Me(H_2O)_6]^{2+} + 4\ L + 2\ Cl^- \leftrightarrow [MeL_4(H_2O)_2]Cl_2 + 2\ H_2O \quad (3)$$
wherein L is the extractant molecules.

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The coordination number change is compelled by large inorganic ligands (such as Cl⁻, Br⁻, I⁻, SCN⁻) or organic ligands, for instance, by derivatives of pyridine, though most of all by derivatives of imidazole, substituted in position 2 or 4 [18-23].

The Pd(II) cation forms flat 4-coordination complexes. According to Ma and Freisera [28], the process of complexing Pd(II) that occurs in the aqueous phase with the oxime derivatives (L) can be described by the equations:

$$[PdCl_4]^{2-} \leftrightarrow [PdCl_3]^- + Cl^- \quad (4)$$
$$[PdCl_3]^- + HL \leftrightarrow [PdCl_2L]^- + Cl^- + H^+ \quad (5)$$
$$[PdCl_2L]^- + HL \leftrightarrow [PdL_2] + 2Cl^- + H^+ \quad (6)$$

The stable complex formed in the reaction (6) is solvated by molecules of the solvent (S) and passes into the organic phase in the form of flat 4-coordination complexes (Equation 7).

$$[PdL_2] + 2S \leftrightarrow [PdL_2S_2] \quad (7)$$

The following conditions must be satisfied before a metal cation can be transferred from the aqueous into the organic phase:

– maximum reduction of the cation's load,
– maximum dehydration of the cation,
– increased volume of the cation being transferred.

For a suitably selected extractant, all these requirements are satisfied. Such extractants include anionic chelating organic ligands, e.g., α-hydroxyoximes [29].

In the case of molecular ligands (e.g., alkylimidazoles), complexes which contain salt anions (chloride, nitrate etc.) balancing the cation's load pass into the organic phase.

It was the objective of this paper to investigate the possibility of separation of Pd(II) ions from a mixture of Co(II), Ni(II), Cu(II) and Pd(II) ion from aqueous chloride solutions by solvent extraction in which 1-hexyl-2-methylimidazole was the extractant. Chloroform was used as a water non-miscible solvent. The tests were carried out at a temperature of 25°C at a constant strength of the aqueous solution of I = 0.5, as maintained by the KCl solution. 1-Hexyl-2-methylimidazole was used as the carrier in polymer inclusion membranes for the separation of Co(II), Ni(II), Cu(II) and Zn(II) ions [30,31].
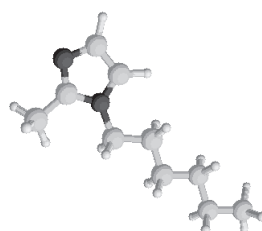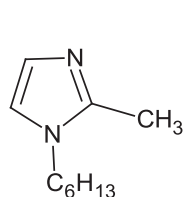
Experimental

Reagents

1-Hexyl-2-methylimidazole (synthesis [32]) was used as an individual model extractant. Its structure is shown in Fig. 1. Chlorides of copper(II), palladium(II), cobalt(II), nickel(II), potassium, hydrochloric acid and chloroform (POCh, Gliwice, Poland) were of analytical grade.

Extraction procedure

Aqueous solutions containing two, three, and four metal ions from the group comprising Cu(II), Pd(II), Co(II) and Ni(II) were prepared in measuring flasks. The concentration of each metal ion in the mixtures was 10 mM. The concentration of hydrochloric acid in all of the aqueous solutions was 20 mM. A constant ionic strength of 0.5 was maintained in all of the aqueous solutions, by adding a suitable quantity of potassium chloride.

A starting organic solution, containing 0.1 mol/dm³ of 1-hexyl-2-methylimidazole in chloroform, was prepared in a measuring flask. The organic solution was mixed with a pure solvent at different volume ratios so as to obtain 11 samples having different extractant concentrations.

Equal volumes of the aqueous and organic solutions were placed in calibrated test tubes with a ground stopper. The extraction process was carried out in a thermostated shaker (type 357, Elpan-Poland) at a temperature of 25°C. After achieving the partition equilibrium during a maximum of 30 minutes the phases were separated. The phases were observed for any change in volume. The aqueous phase was measured for pH (digital pH-meter Mettler-Lab PHM 250, Radiometer with a combined electrode, pH C2401-81) and for concentration of its other metal ions using spectrophotometry (spectrophotometer AAS BUCK Scientific 210 VGP).

Results and Discussion

The alkyl derivative of imidazole substitute in position 2 of the extractant causes a strong steric effect, making difficult the formation of octahedral complexes, though its interference with the formation of 4-coordination bonds is less significant. This type of hydrophobic ligands can be used sufficiently as extractants, which facilitate the extraction of Cu(II), Co(II) or Pd(II).

b.p.
131-135°C/2 mmHg

pK_a 8.32 [33]

Fig.1. Structure of 1-hexyl-2-methylimidazole molecule

Table 1. Stability constants of the test metal complexes (log βn) with 1-hexyl-2-methylimidazole and their partition co-efficients (Pn) between the aqueous phase and chloroform at a temperature of 25°C at an ionic strength of the aqueous phase of 0.5 (KNO_3 and HNO_3)

metal ions	stability constants				partition coefficients			
	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	P_1	P_2	P_3	P_4
Co(II)[34]	1.73	2.08	2.76	3.65	0.5	21	64	90
Ni(II)[35]	0.37	1.21	1.87	2.46	0.4	1.2	2.8	4.5
Cu(II)[36]	3.52	4.63	6.98	7.53	2.7	35	120	285
Pd(II)[37]	1.29	1.96	2.49	3.11	12	70	180	326

Stability constants (log βn) of the test metal complexes with 1-hexyl-2-methylimidazole and their partition coefficients (Pn) between the aqueous phase and chloroform are shown in Table 1.

From the data in Table 1, it can be seen that the stability constants of complexes of 1-hexyl-2-methylimidazole in the same stage of complexation (n = const.) decreased in the series: Cu (II)> Co (II)> Pd (II) > Ni (II). For all types of complexes of the test metals, the partition coefficients (Pn) are the highest for Pd(II), then for Cu(II) and Co(II), and the lowest for Ni(II) ions.

A hexyl substitute, bound in position 1 with imidazole molecule intensifies the extractant's hydrophobic properties and facilitates extraction of the complexes into the organic phase. A methyl substitute in position 2 constitutes a steric hindrance making it difficult to form the octahedral complexes of Ni(II) and Co(II).

The phenomenon is best observable for Ni(II), of which the complexes are the least stable (Table 1). The steric effect, as well, hinders the formation of Co(II) complexes with 1-hexyl-2-methylimidazole although, in this case, primarily in the fourth step of complexation, the coordination number of the central ion will change from 6 to 4 according to the equation:

$$[Co(H_2O)_6]^{2+} + nL \leftrightarrow [Co(H_2O)_{4-n}L_n]^{2+} + (2+n)H_2O \qquad (8)$$

The symmetry of the coordination sphere is changed from octahedral to tetrahedral. Tetrahedral complexes are much more easily extracted, compared with octahedral ones. The stability of Cu(II) complexes is also weakened by the steric effect, although the Jahn-Teller effect is distorted due to its coordination sphere, thus becoming less sensitive to the extractant's steric hindrance which, in consequence, enables extraction of the metal. Pd(II) forming flat-square complexes according to Equations (4-7), is easily extracted, as evidenced by the highest partition coefficients (P_3 and P_4) (Table 1).

Based on analytic determinations, using Formula (9), the authors calculated metal extraction percentages (%E) for all ion mixtures as well as pH values of the aqueous phase.

$$\%E = \frac{C_M^0 - C_M}{C_M^0} \cdot 100\% \qquad (9)$$

In Formula (9) C_M and C_M^0 denote, respectively, the metal's equilibrium concentration in the aqueous phase and its analytical (initial) concentration. Graphs showing a relationship between % E vs. the pH of the aqueous phase for the binary mixtures (Pd-Ni, Pd-Co, Pd-Cu), for the ternary mixtures (Pd-Co-Ni, Pd-Cu-Ni, Pd-Co-Cu), and for the quaternary mixture (Pd-Ni-Co-Cu) are provided in Figures 2-4.

It can be seen in Figures 2-4 that the extraction percentage for each of the test metals between the aqueous and organic phases tends to increase with the extractant's increasing concentration in the aqueous phase, thereby it increases with an increasing pH of the aqueous phase and depends on the type of metal. The extraction percentage decreases in the following order: Pd(II) > Cu(II) > Co(II) > Ni(II). Its highest value is observed for the Pd(II) ions in the binary mixtures containing Ni(II) or Co(II); it is 84% for pH=7.9 and 76% for pH=7.7, respectively. In the case of the ternary mixtures, the extraction percentage for Pd(II) reaches 70-72% (for pH in the range 7.1-7.4), while in the case of the quaternary mixture, it is not higher than 70% (for pH 7.33). The extraction percentage for Cu(II) ions in the test mixtures varies between 40 and 50%. Practically, only a small percentage of the Co(II) and Ni(II) ions pass into the organic phase (not more than 19% and 5%, respectively).

Figures 2-4 indicate that separation of Pd(II) ions is possible for each type of mixture (binary, ternary, or quaternary). A decrease in the Pd(II) extraction percentage in the order: binary mixtures < ternary mixtures < quaternary mixture may be due to the formation of multiple core complexes, which are less likely to pass into the organic phase.

Using Formula (10), selectivity coefficients were calculated for the separation of the respective ions in the binary and ternary mixtures and for the quaternary mixture; their values are provided in Table 2.

$$S_{Me1/Me2} = \frac{\%E_{Me1}}{\%E_{Me2}} \qquad (10)$$

The data in Table 2 indicate that, in the solvent extraction process in which the extractant used is 1-hexyl-2-methylimidazole dissolved in chloroform, it is easiest to separate Pd(II) ions from a Pd-Ni mixture and hardest – to separate Pd(II) from Cu(II), although it is still possible, and easier to do at lower pH values.
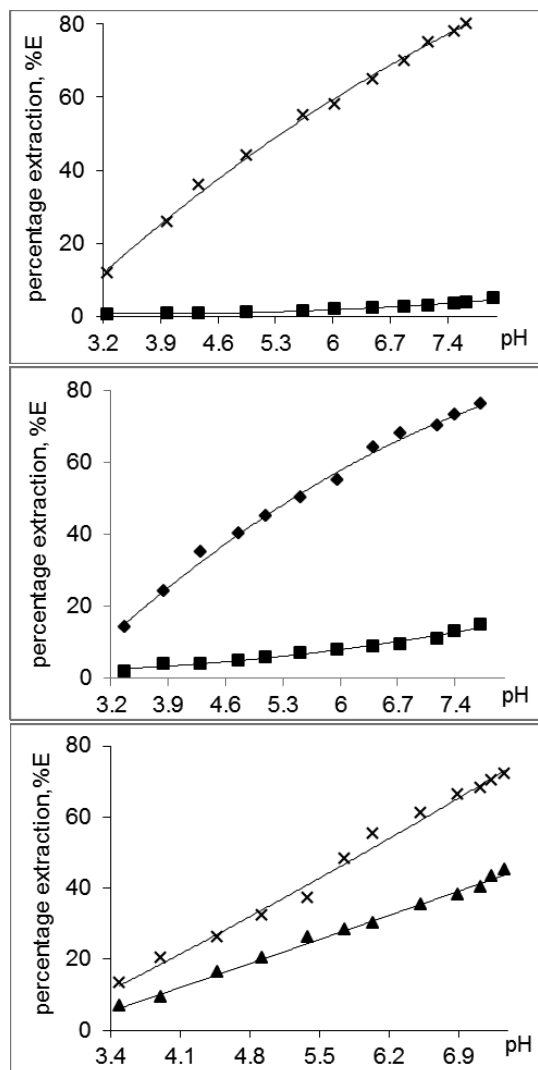
Fig. 2. Percentage of metal ion extraction from chloride solutions having the ion strength of 0.5 (KCl), vs. pH of the aqueous phase for binary mixtures, temperature 25oC, extractant: 1-hexyl-2-methylimidazole in chloroform. x – Pd(II), ■ – Ni(II), ▲ – Cu(II), ♦ – Co(II)

Fig. 3. Percentage of metal ion extraction from chloride solutions having the ion strength of 0.5 (KCl), vs. pH of the aqueous phase for ternary mixtures: temperature 25°C, extractant: 1-hexyl-2-methylimidazole in chloroform. x – Pd(II), ■ – Ni(II), ▲ – Cu(II), ♦ – Co(II)

Separation coefficients for Pd(II) depending on the mixture compositions, tend to decrease in the following order: binary mixtures < ternary mixtures < quaternary mixture.

In the quaternary mixture, the highest separation coefficients were obtained for the systems: Pd(II)/Ni(II), Pd(II)/Co(II); at a pH 5.4 of the aqueous phase, they are: 13.3 and 7.7, respectively.

Conclusions

Solvent extraction in a liquid-liquid system can be an effective method for the separation of metal ions, Pd(II) from Cu(II), Co(II) and Ni(II). Using 1-hexyl-2-methylimidazole as extractant, and chloroform as a water non-miscible solvent, 70% of palladium can be extracted at pH 7.33 from a quaternary mixture in a single step.
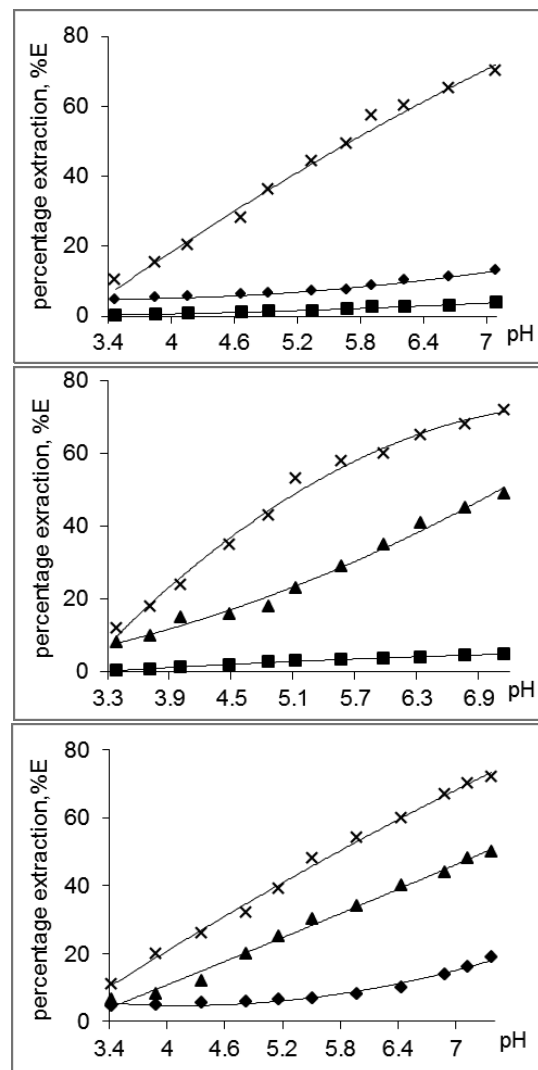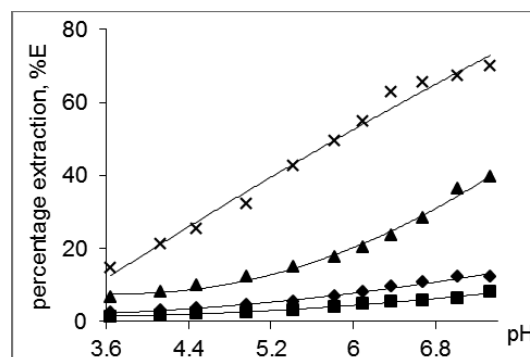

Fig. 4. Percentage of metal ion extraction from chloride solutions having the ion strength of 0.5 (KCl), vs. pH of the aqueous phase for quaternary mixtures system {Pd(II)-Ni(II)-Co(II)-Cu(II)}: temperature 25°C, extractant: 1-hexyl-2-methylimidazole in chloroform. x – Pd(II), ■ – Ni(II), ▲ – Cu(II), ♦ – Co(II)

Table 2. Co(II), Ni(II), Cu(II), and Pd(II) ion separation coefficients, vs. pH of the aqueous phase in solvent extraction: temperature of 25oC, extractant: 1-hexyl-2-methylimidazole, solvent: chloroform

Separation selectivity $S_{Me1/Me2}$											
Pd(II)/Ni(II) system											
pH	3.25	3.98	4.36	4.95	5.64	6.02	6.49	6.87	7.17	7.48	7.63
$S_{Pd(II)/Ni(II)}$	17.14	28.89	36.00	36.67	34.38	29.00	27.08	25.00	25.00	22.29	20.00
Pd(II)/Co(II) system											
pH	3.37	3.84	4.29	4.76	5.09	5.51	5.96	6.4	6.73	7.18	7.4
$S_{Pd(II)/Co(II)}$	7.00	6.00	8.75	8.00	7.50	7.14	6.88	7.11	7.16	6.36	5.62
Pd(II)/Cu(II) system											
pH	3.49	3.91	4.47	4.92	5.38	5.76	6.04	6.52	6.89	7.12	7.23
$S_{Pd(II)/Cu(II)}$	2.00	2.22	1.63	1.60	1.42	1.71	1.83	1.74	1.74	1.70	1.63
Pd(II)/Ni(II)/Co(II) system											
pH	3.47	3.85	4.16	4.67	4.93	5.34	5.68	5.91	6.22	6.65	7.09
$S_{Pd(II)/Ni(II)}$	33.33	30.00	25.00	25.45	27.69	29.33	24.50	21.92	21.43	21.67	17.95
$S_{Pd(II)/Co(II)}$	2.17	3.00	3.64	4.59	5.54	6.29	6.62	6.71	6.00	5.91	5.38
Pd(II)/Ni(II)/Cu(II) system											
pH	3.39	3.72	4.015	4.49	4.86	5.13	5.57	5.98	6.34	6.77	7.15
$S_{Pd(II)/Ni(II)}$	24.00	22.50	20.00	17.50	15.93	17.67	16.57	15.79	16.25	15.11	14.40
$S_{Pd(II)/Cu(II)}$	1.50	1.80	1.60	2.19	2.39	2.30	2.00	1.71	1.59	1.51	1.47
Pd(II)/Co(II)/Cu(II) system											
pH	3.42	3.89	4.36	4.82	5.16	5.51	5.97	6.43	6.88	7.12	7.37
$S_{Pd(II)/Co(II)}$	2.44	4.00	4.73	5.33	6.00	6.86	6.75	6.00	4.79	4.38	3.79
$S_{Pd(II)/Cu(II)}$	1.69	2.50	2.17	1.60	1.56	1.60	1.59	1.50	1.52	1.46	1.44
Pd(II)/Ni(II)/Co(II)/Cu(II) system											
pH	3.64	4.13	4.48	4.97	5.42	5.82	6.09	6.37	6.68	7.01	7.33
$S_{Pd(II)/Ni(II)}$	10.89	12.40	11.30	12.90	13.26	12.64	11.62	11.42	11.17	10.45	8.77
$S_{Pd(II)/Co(II)}$	6.17	7.24	6.92	7.26	7.66	7.16	6.85	6.58	6.14	5.52	5.67
$S_{Pd(II)/Cu(II)}$	2.23	2.63	2.55	2.65	2.82	2.82	2.71	2.66	2.30	1.86	1.76

The structure of the 1-hexyl-2-methylimidazole molecule as well as its complex forming properties enable the separation of Pd(II), Cu(II), Co(II) and Ni(II) ions, as indicated by the separation coefficients.

Chances are that similar effects can be attained in other polar solvents.

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