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Ion-Exchange Sorption of Silver(I) Chloride Complexes from Aqueous HCl Solutions

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Abstract—The ion-exchange sorption of silver(I) chloride complexes from 1−4 M aqueous solutions of HCl on a series of Purolite anionites with various functional groups was studied. The ion-exchange equilibria in the systems were found to be anomalous according to Raman spectroscopy, which does not significantly affect the sorption properties of the ionites.

In recent years, the constantly increasing demand for precious metals has stimulated growth of their production. The most important source of precious metals in Russia in the nearest future will be the large-scale gold ore objects in carbonaceous-terrigenous black-shale strata extending from Yenisei to Chukotka [1, 2]. These ores account for ~14% of the world's gold reserves and contain silver, platinum, and palladium in industrial concentrations (0.5−1 g/t), so their extraction together with gold certainly shows great promise [1].

A promising method for complex processing of gold−platinum ores is hydrochlorination; it has certain advantages over cyanation from the viewpoint of not only ecology, but also dissolution rate [3−6]. Hydrochlorination forms chloride complexes of noble metals, which differ in stability and chemical inertness [7, 8]. Further extraction from solutions is conveniently performed by sorption methods [2, 7, 9].

Both the ionic state of platinum metals and gold in hydrochloric acid and chloride solutions and their sorption extraction from these media are well defined [7, 8, 10−12]. As for silver chloride complexes, their formation and thermodynamic properties were studied relatively long ago [13, 14], but there are no data on their sorption extraction. During the last 10 to 15 years, research has concentrated on silver sorption from thiosulfate, thiocyanate, or ammonia solutions or mixed silver complexes [15]. Nevertheless, investigation of sorption extraction of silver chloride complexes is very important because, as mentioned above, silver accompanies platinum, palladium, and gold in black-shale ores and secondary sources (e.g., electronic waste), and these materials are processed by

hydrochlorination. Therefore, the goal of the present study was to investigate the ion-exchange extraction of silver(I) chloride complexes.

EXPERIMENTAL

For purposes of this study, Purolite ionites with different functional groups were chosen. Their physicochemical characteristics are given in Table 1. Before use, all the sorbents were prepared by conventional techniques and transferred to the Cl⁻ form. As follows from the given data, the objects of investigation were strongly and weakly basic anionites and sorbents of complexing type. Note that the Purogold™ A 193 anionite has not been studied earlier. The manufacturer offers this sorbent for gold extraction from solutions and pulps, due to which the ionite has increased mechanical strength.

The starting solutions of silver(I) chloride complexes were prepared by dissolving exact silver nitrate samples ("ch.d.a." (analytical) grade) in 1, 2, or 4 M HCl. To verify the completeness of complexation, a qualitative Ag$^+$ test was performed with potassium hydroorthophosphate in a separate small portion of the solution (if the complexation was incomplete, the solution became yellow) [16]. The silver concentration in the initial solutions (7.1 mmol/L) was determined by potentiometric titration with a silver indicator electrode and silver chloride reference electrode [17].

The silver(I) concentration in the hydrochloric acid contacting solutions was determined by spectrophotometry with bromopyrogallol red [17]. The ionic state of silver in the solutions was controlled by record-

Table 1. Physicochemical characteristics of ionites based on St−DVB

Ion exchanger grade	Type	Physical structure	Functional groups	Exchange capacity rel. to the Cl⁻ ion, mmol/g	Hygroscopicity, %	Swelling capacity, %	Bulk mass, g/cm³
Purolite S 985	Complexing anionite	MP	PAGs, $-CH_2-NH_2$; $-CH_2-CH=NH$; $-CH_2-N(CH_3)_2$	2.3	52−57	20	0.67−0.71
Purogold™ S 992	Polyacrylic complexing anionite	MP	CA, $-CH_2-N^+(CH_3)_3$; $-CH_2-N(CH_3)_2$	4.4	47−55	−	0.65−0.69
Purogold™ A 193	Mixed type anionite	MP	QAB, TAGs, $-CH_2-N^+(CH_3)_3$; $-CH_2-N(CH_3)_2$	3.8	46−56	22	0.65−0.66
Purolite A 500	Highly basic anionite of type I	MP	QAB, type I, $-CH_2-N^+(CH_3)_3$	1.2	57−63	20	0.67−0.70
Purolite A 300	Highly basic anionite of type II	G	QAB, type II, $-CH_2-N^+(CH_3)_2$ CH_2-CH_2-OH	1.4	40−45	10	0.69−0.72
Purolite A 111	Weakly basic anionite	MP	TAGs, $-CH_2-N(CH_3)_2$	1.7	56−62	40	0.64−0.68

St, styrene; DVB, divinylbenzene; MP, macroporous; G, gel; PAGs, polyamine groups; MAs, mixed amines; QAB, quaternary ammonium base; and TAGs, tertiary amino groups.

ing the electronic absorption spectra in the wavelength range 190−700 nm on a Specol 1300 spectrophotometer (Carl Zeiss Jena-Analytik Jena).

Silver sorption from the 1−4 M HCl solutions was performed under the static conditions at a ratio of solid to liquid phases of 1 : 100 and a temperature of 20 ± 1°C. The equilibrium set-in time was determined in a special experiment and was 24 h. We also preliminarily determined the stability of the silver chloride complexes, which was 48 h. The exchange capacity (EC) of the sorbents, degree of extraction of silver complexes (R), and distribution coefficients (D) were calculated from the obtained data. The sorption isotherms were constructed by varying the molar ratio of the ionite to the amount of silver(I) ions in the contacting solution [18−20]. The apparent ion-exchange equilibrium constants $K_{1,2}$ (L/mol) were calculated from the obtained isotherms according to the mass action law [18, 20].

The Raman spectra of the ionites were recorded on an RFS 100/S Bruker Raman-Fourier spectrometer. The spectra were obtained as a result of 300 scans in the range 100−3500 cm⁻¹.

The kinetic properties of ionites during the extraction of silver(I) chloride complexes were studied by the "limited volume" method [18, 20, 21]; the kinetic parameters (half-exchange time, diffusion coefficients) were calculated based on the results of this study.

The desorption of the silver(I) chloride complexes after their extraction from solution with anionites was performed with 1−5% ammonia solutions.

All the results were statistically processed. The average error for three parallel measurements did not exceed 6%.

RESULTS AND DISCUSSION

As mentioned above, the solubility of silver(I) chloride and its transformation into chloride complexes were studied in [13, 14, 17, 22, 23]. According to these data, silver is probably present in the 1−4 M hydrochloric acid solutions in the form of $[AgCl_2]^-$ because under these conditions the formation function is $n = 2.05$, and the fraction of the complex form of the metal relative to its total concentration is $\alpha(MeL_2) = 0.82$ [13, 22, 23]. In the absorption spectra of the initial hydrochloric acid solutions of silver(I) recorded in our study, the absorption maximum lies at a wavelength of 195 nm (for 1 M HCl) and 200 nm (for 2 and 4 M HCl), which also corresponds to the above complex [17]. Thus, the use of anionites for extracting silver(I) from hydrochloric acid solutions seems justified.

The data on sorption extraction of silver chloride complexes at different HCl concentrations in contacting solutions are given in Table 2. As follows from Table 2, the sorption capacity of the ionites with respect to silver(I) chloride complexes in 1 M HCl is very high, especially in the strongly basic anionites A 500 and A 300 and polyamine sorbent S 985 (degree of extraction is more than 70−80%). The sorption capacity of the weakly basic anionite A 111 and complexing anionite with the functional groups of mixed amines

Table 2. Sorption extraction of silver(I) from hydrochloric solutions (C_0(Ag) = 2.0 mmol/L)

| Ion exchanger grade	Parameters of sorption	C_0(HCl), M		
		1.0	2.0	4.0
Purolite S 985	R, %	82.1 ± 3.3	71.8 ± 2.9	57.1 ± 2.3
	log D	1.66 ± 0.083	1.40 ± 0.071	1.12 ± 0.056
Purogold™ S 992	R, %	55.8 ± 2.2	–	7.7 ± 0.31
	log D	1.10 ± 0.055	–	0.26 ± 0.013
Purogold™ A 193	R, %	68.5 ± 3.4	86.3 ± 4.3	79.1 ± 3.2
	log D	1.34 ± 0.081	1.81 ± 0.091	1.58 ± 0.063
Purolite A 500	R, %	84.0 ± 4.2	84.8 ± 3.4	75.2 ± 3.1
	log D	1.72 ± 0.086	1.75 ± 0.088	1.48 ± 0.095
Purolite A 300	R, %	70.1 ± 3.5	23.0 ± 1.2	–
	log D	1.37 ± 0.068	0.47 ± 0.024	–
Purolite A 111	R, %	55.8 ± 2.7	–	50.7 ± 2.5
	log D	1.10 ± 0.061	–	1.01 ± 0.051

Purogold™ S 992 was lower. As the hydrochloric acid concentrations in the contacting solutions increased to 2 and 4 M, the sorption capacity of the anionites decreased, which can probably be explained by the increased competitive effect of the chloride ions. Note that the sorption capacity of the new Purogold™ A 193 sorbent does not decrease even under the conditions of 4 M HCl, which can open up prospects for selective separation of silver(I) ions accompanying the platinum metal ions.

Then the isotherms of sorption of silver(I) chloride complexes from hydrochloric acid solutions on the ionites under study were obtained, which are anomalous regardless of the type of functional groups of the sorbents. Figures 1 and 2 show the isotherms for the Purolite S 985 and Purogold TM A 193 anionites, respectively. The first isotherm is a curve with a hys-

teresis, and the second is a broken stepped curve. The sorption isotherms on other anionites under study are similar.

Note that the anomalous form of sorption isotherms was described for inorganic exchangers, carbon adsorbents, and cation exchangers [20, 24–26]. Anomalous sorption isotherms are characteristic for ionites having several types of functional groups, suggesting that the character of exchange isotherms is related to the structure of the ionite [26, 27]. It is believed that phase transformations associated with a rearrangement of the polymer framework can occur during ion exchange. This is described either by jump-like isotherms or by hysteresis [26].

In addition, for swelling ionites, the hysteresis can be related to the dependence of swelling on the contact time and solution concentration. The higher the con-
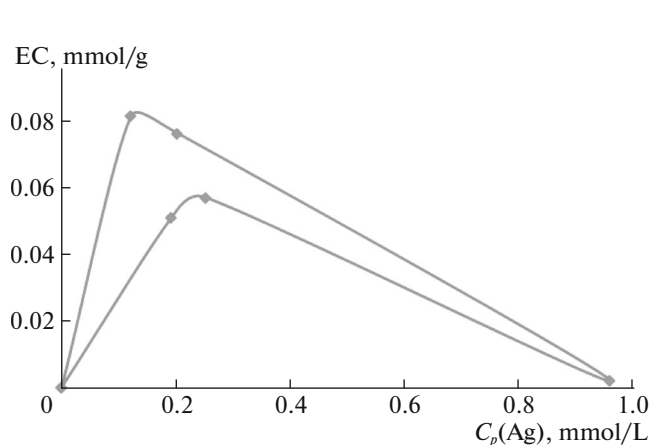
Fig. 1. Isotherm of sorption of silver(I) chloride complexes from the 4 M HCl solution on the Purolite S 985 anionite.
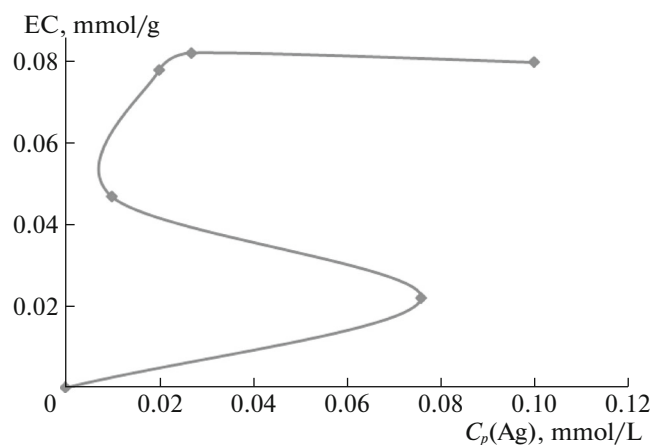
Fig. 2. Isotherm of sorption of silver(I) chloride complexes from the 4 M HCl solution on the Purogold™ A 193 anionite.
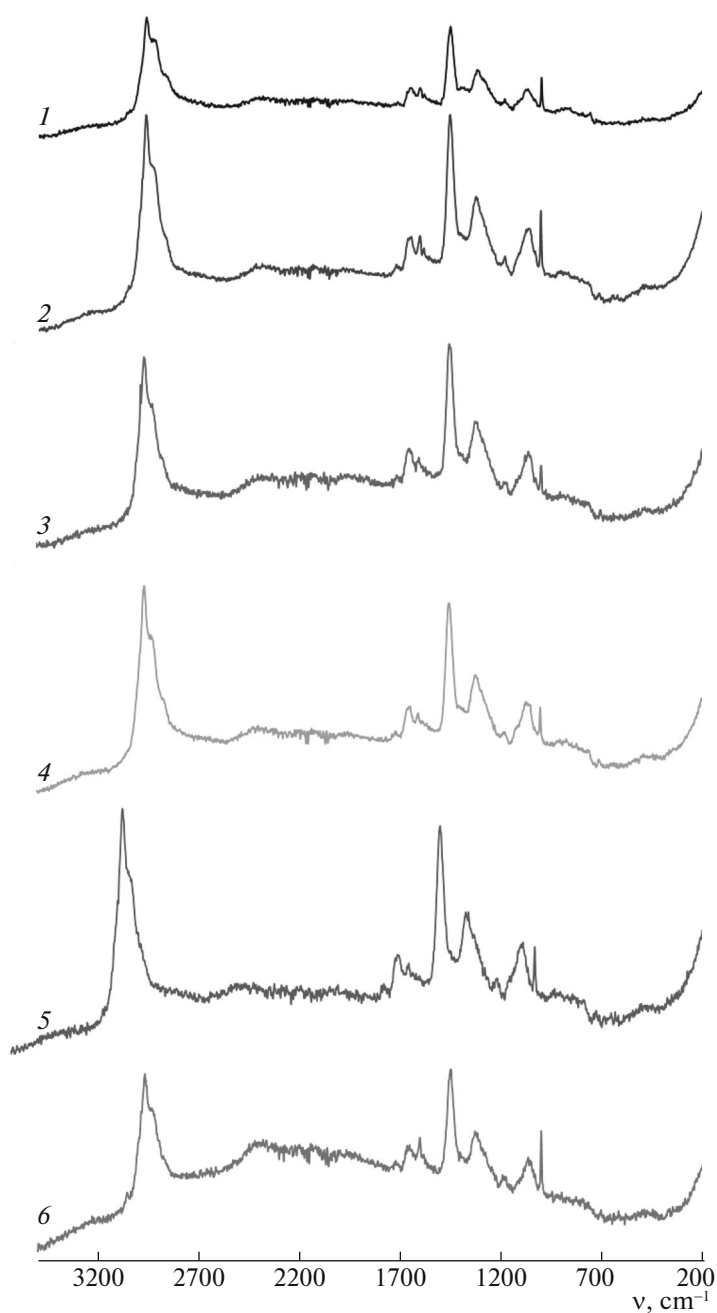
Fig. 3. Fragments of the Raman spectra of the Purolite S 985 anionite (*1*) in the starting Cl⁻form and (*2–6*) saturated with silver(I) chloride complexes with silver concentrations (mmol/L) of (*2*) 0.30, (*3*) 0.48, (*4*) 0.80, (*5*) 0.85, and (*6*) 0.95; $C_0(HCl) =$ 4.0 M.

centration of the contacting electrolyte, the stronger the compression of the ionite, which leads to the narrowing of the sorbent pores and slows the ion exchange process [26]. Consequently, these anomalous phenomena during ion exchange require detailed studies; therefore, we recorded the Raman spectra of Purolite S 985 ionite samples in the initial chloride form and after saturation with silver(I) chloride complexes corresponding to each point of the obtained isotherm. Figure 3 shows the fragments of these spectra.

In the spectra of ionite samples saturated with silver(I) chloride complexes, a peak at 268 cm⁻¹ appears, which corresponds to the vibrations of the N → Ag bonds or is due to the presence of $[AgCl_2]^-$ anions in the ionite phase [28]; the intensity of these peaks varies and depends on the silver concentration. Note that spectrum *4* corresponding to the point of the isotherm located virtually on the abscissa axis (Fig. 1) does not contain the 268 cm⁻¹ peak. The obtained spectra

Table 3. Apparent ion-exchange equilibrium constants ($K_{1,2}$, L/mol) during the extraction of silver(I) chloride complexes, C_0(HCl) = 4.0 M

Ion exchanger grade	C_0(Ag (I)), mmol/L	$K_{1,2} \times 10^{-3}$	Ion exchanger grade	C_0(Ag(I)), mmol/L	$K_{1,2} \times 10^{-3}$
Purolite S 985	0.30	9.28	Purolite A 500	0.30	0.069
	0.48	5.11		0.48	3.84
	0.80	—		0.80	6.67
	0.85	1.60		0.85	6.60
	0.95	1.14		0.90	6.02
Purogold™ A 193	0.30	0.43	Purolite A 111	0.30	0.57
	0.48	1.21		0.80	2.01
	0.80	2.01		0.85	2.25
	0.85	2.11		0.90	1.91
	0.90	1.87		0.95	1.43

exhibit peaks in the range 700–750 cm^{-1} corresponding to the stretching vibrations of C−Cl bonds [29].

All the spectra of the ionite samples saturated with silver chloride complexes show changes in the intensities of the peaks at 1000 cm^{-1} corresponding to the vibrations of the benzene rings compared with the spectrum of the ionite in the chloride form (spectrum *1*, Fig. 3) [29]. All the Raman spectra of the samples saturated with chloride complexes show an increase in the peak intensities in the ranges 2845–2870, 2915–3000, and 1200–1450 cm^{-1} relative to the spectrum of the initial sample, which characterizes the changes in the alkyl groups of the polymer chain [30].

Thus, based on the Raman spectroscopic study of Purolite S 985 anionite, we can conclude that the structure of the polymer framework of the sorbent changes, and the stereochemical effects give rise to an anomalous sorption isotherm. According to [24, 26, 27], these anomalous sorption isotherms cause difficulties in calculations of the apparent ion-exchange equilibrium constants because these quantities change depending on the degree of ionite saturation with the sorbed ions. Therefore, we calculated the apparent ion-exchange equilibrium constants for the extraction of silver(I) chloride complexes for each point of the sorption isotherms obtained for the anionites. The results are given in Table 3.

According to the given data, the values of the constants indicate that the ionites under study are selective with respect to the extracted silver(I) chloride complexes despite the anomalous ion-exchange process. For the industrial use of ionites with only part of the exchange capacity used, however, these anomalies are irrelevant [26].

Then the kinetic properties of the Purolite S 985 anionite were studied. At first we determined that the kinetics was of intraparticle diffusion type according to the classic Boyd's model [18, 20, 21], and then the kinetic parameters were calculated: the half-exchange

time was 45 s, and the average effective diffusion coefficient 9.95×10^{-6} cm^2/s. As follows from these data, the Purolite S 985 anionite possesses good kinetic properties, as evidenced by both the order of the diffusion coefficient and the short half time of exchange.

We also examined the possibility of desorption of silver chloride complexes after their extraction with the ionites under study. For this purpose, we at first chose a 5% ammonia solution. The choice of desorbent was dictated by its interaction with silver ions to form ammonia complexes, whose stability exceeds that of silver chloride complexes by several orders of magnitude [31]. The degree of silver extraction was ~100%. Subsequently the desorbent concentration was decreased to 1%, and silver extraction was also ~100% from all the anionites under study.

Thus, based on the data obtained, it can be concluded that ion-exchange extraction of silver(I) from hydrochloric acid solutions on anionites is possible despite the anomalous character of the ion-exchange equilibrium.

ACKNOWLEDGMENTS

REFERENCES

1. *Mineral Raw Materials: From Subsoil to Market. Noble Metals and Diamonds. Gold, Silver, Platinoids, and Diamonds,* Ed. by A. P. Stavskii (Nauchnyi Mir, Moscow, 2011) [in Russian].
2. G. L. Pashkov and Yu. S. Kononov, in *Proceedings of the 4th International Internet-Symposium on Sorption and Extraction,* Ed. by V. A. Avramenko (Dal'nauka, Vladivostok, 2011), p. 40.
3. V. V. Lodeishchikov, Zolotodobycha **129**, 7 (2009).
4. F. Habashi, J. Min. Met. **45**, 1 (2009).

5. M. A. Meretukov, Tsvetn. Met., No. 12, 54 (2008).

6. I. A. Kakovskii and V. V. Gubailovskii, Tsvetn. Metall. **18**, 139 (1975).

7. Yu. A. Zolotov, G. M. Varshal, and V. M. Ivanov, *Analytical Chemistry of Platinum Group Metals* (Editorial URSS, Moscow, 2003) [in Russian].

8. Yu. N. Kukushkin, *Chemistry of Coordination Compounds* (Vysshaya Shkola, Moscow, 1985) [in Russian].

9. G. L. Pashkov, Yu. S. Kononov, and V. V. Patrushev, in *New Approaches in Chemical Technology of Mineral Raws. Application of Extraction and Sorption, Proceedings of the 2nd Russ. Conference, St. Petersburg* (Kol'sk. Nauch. Tsentr RAN, Apatity, 2013), p. 110.

10. S. I. Ginzburg, N. A. Ezerskaya, I. V. Prokof'eva, et al., *Analytical Chemistry of Platinum Metals* (Nauka, Moscow, 1972) [in Russian].

11. F. E. Beamish, *The Analytical Chemistry of the Noble Metals* (Elsevier, Amsterdam, 1966).

12. F. L. Bernardis, R. A. Grant, and D. C. Sherrington, React. Funct. Polym. **65**, 205 (2005).

13. J. H. Jonte and D. S. Martin, J. Am. Chem. Soc. **74**, 2052 (1952).

14. J. J. Fritz, J. Solution Chem. **14**, 865 (1985).

15. N. S. Bekturganov, D. B. Gogol', M. R. Bisengalieva, A. S. Mukusheva, A. K. Koizhanova, and L. L. Osipovskaya, Russ. J. Inorg. Chem. **59**, 337 (2014).

16. V. N. Alekseev, *Course of Qualitative Chemical Semi-Microanalysis* (Khimiya, Moscow, 1973) [in Russian].

17. I. V. Pyatnitskii and V. V. Sukhan, *Analytical Chemistry of Silver* (Nauka, Moscow, 1975) [in Russian].

18. F. Helfferich, *Ion Exchange* (McGraw-Hill, New York, 1962; Inostr. Liter., Moscow, 1963).

19. N. G. Polyanskii, G. V. Gorbunov, and N. L. Polyanskaya, *Methods of Ionite Study* (Khimiya, Moscow, 1976) [in Russian].

20. Yu. A. Kokotov and V. A. Pasechnik, *Equilibrium and Kinetics of Ion Exchange* (Khimiya, Leningrad, 1970) [in Russian].

21. F. Helfferich, React. Polym. **13**, 191 (1990).

22. J. H. Butler, *Ionic Equilibrium: A Mathematical Approach* (Addison-Wesley, Reading, MA, 1964).

23. V. M. Talanov and G. M. Zhitnyi, *Ionic Equilibria in Aqueous Solutions* (Akad. Estestvoznaniya, Moscow, 2007) [in Russian].

24. *Ionits in Chemical Technology,* Ed. by B. P. Nikol'skii and P. G. Romanov (Khimiya, Leningrad, 1982) [in Russian].

25. *Non-Stoichometric Compounds,* Ed. by K. V. Astakhov (Khimiya, Moscow, 1971) [in Russian].

26. R. Griesbach, *Ionenaustauscher in Einzeldarstellungen* (Akademie, Berlin, 1957) [in German].

27. G. V. Samsonov, *Ion Exchange and Ionits* (Nauka, Moscow, 1970) [in Russian].

28. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Mir, Moscow, 1991; Wiley, New York, 1986).

29. L. A. Kazitsina and N. B. Kupletskaya, *Application of UV-, IR-, NMR-, and Mass Spectroscopy in Organic Chemistry* (Mosk. Gos. Univ., Moscow, 1979) [in Russian].

30. K. M. Saldadze and V. D. Kopylova-Valova, *Complexing Ionits* (Khimiya, Moscow, 1980) [in Russian].

31. Yu. Yu. Lur'e, *Handbook in Analytic Chemistry* (Khimiya, Moscow, 1979) [in Russian].

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