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Ion Exchange Equilibria in Simultaneous Extraction of Platinum(II, IV) and Rhodium(III) from Hydrochloric Solutions

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Abstract—Regularities of sorption extraction of platinum(II, IV) and rhodium(III) by anion exchangers of various physical and chemical structure in the presence of hydrochloric media were studied. It is established that AM-2B, Purolite A 500, and Purolite S 985 ionites adsorb complex anions of platinum metals employing mixed mechanism. A high affinity of the studied anionites for the studied complex anions of platinum and rhodium is established.

Keywords: platinum, rhodium, ionites, ion exchange equilibria, hydrochloric acid solutions, sorption. **DOI**: 10.1134/S0036024412060192

INTRODUCTION

Sorption methods using anionites have been successfully used to extract the platinum metals from hydrochloric acid media [1, 2]. Sorption of platinum metals is usually carried out from solutions obtained by the decomposition of materials containing precious metals. Transfer of such samples to solution is carried out using various techniques: dissolving in acids, chlorination, melting, and other methods [3-6]. In the end result the obtained solutions contain complexes of platinum metals with different stability and chemical inertness, which are subject to hydrolysis and aquatation [7, 8]; this complicates the sorption of metals, as many valuable components might be lost. For this reason, a high selectivity of the sorbents is very important. Nitrogen-containing anionites that are often used for the extraction of platinum metals usually extract rhodium and platinum by means of ion exchange between the complex anions of Pt and Rh and counterions of the sorbent, as well as by the mechanism of complex formation between the nitrogen atoms of the sorbents functional groups and metal atoms [9].

Calculation of the ion-exchange equilibria in the studied systems is necessary for the successful application of ionites. Even though the hydrochloric acid media of platinum metals have been studied in detail, ion-exchange equilibria in the simultaneous presence of platinum and rhodium remain virtually uninvestigated.

In this work, we study the ion-exchange equilibria in the process of extraction of chloride complexes of platinum(II, IV) and rhodium(III) by anionites that have different physical and chemical natures. At the same time, the pH of contacting solutions is varied over a wide range, since, even though strongly acidic solutions (e.g., spent catalysts) are distributed to a large extent in an industrial environment, aged solutions of noble metals occupy a prominent position in which in the processes of so-called aging (the formation of aqua- and hydroxocomplexes) are observed in a weakly acidic medium.

EXPERIMENTAL

We studied macroporous anionites synthesized by Purolite (S 985 and A 500), and AM-2B sorbent produced in Russia that is successfully used to extract gold in an industial environment. Purolite S 985 contains polyamine functional groups, Purolite A 500 contains quaternary ammonium bases, and AM-2B contains tertiary amino groups and quaternary ammonium bases. We selected these sorbents from the wide range of ionites chosen for a preliminary study, since they exhibited the best sorption properties relative to noble metals. In addition, the Purolite anionites have barely been studied with respect to the sorption of platinum metals.

The initial working solution with a platinum concentration of 9.669 mmol/L in 6 M HCl was prepared by dissolving accurately weighed hexachloroplatinum acid in a small amount of concentrated hydrochloric acid and diluting the solution with water [10].

The initial solution with rhodium concentration of 9.709 mmol/L in 6 M HCl was prepared by the sintering of metallic rhodium sample (0.25 g) with a fivefold

quantity of BaO_2 [8]. The content of rhodium in the resulting solution was determined gravimetrically using thiourea and sulfuric acid [8].

To confirm the ionic states of platinum and rhodium in the studied solutions, electronic absorption spectra in the wavelength range of 190–700 nm were recorded on a CARY 100 Scan spectrophotometer.

Sorbents were preconditioned and converted to the chloride form using standard methods [11]. Sorption of noble metals was performed from hydrochloric acid solutions of different concentrations (0.01-2.0 mol/L). The initial concentration of platinum and rhodium in these solutions was 0.25-0.5 mmol/L.

To plot sorption isotherms using the molar ratios of ionites and sorbents, samples of 0.1 g mass were brought into contact with various amounts (10-75 mL) of working solutions of platinum and rhodium and then left for 24 h to reach equilibrium. Ionites were then separated, and the equilibrium concentration of platinum(II, IV) and rhodium(III) in solution was determined spectrophotometrically with tin(II) chloride. The exchange capacity (OE) was calculated using the obtained data. Compliance of the obtained platinum sorption isotherms in the presence of rhodium to the Langmuir equation was estimated by linearization from the correlation of the function with a linear function:

$$OE = OE_{\infty} + \frac{KC_p}{1 + KC_p},$$
(1)

$$\frac{1}{OE} = \frac{1}{OE_{\infty}} + \frac{1}{OE_{\infty}K}\frac{1}{C_{p}},$$
(2)

where OE_{∞} is the maximum exchange capacity, mmol/g; and *K* is the apparent equilibrium constant of the sorption process, L/mmol.

In the case of rhodium sorption isotherms in the presence of platinum, the apparent ion-exchange equilibrium constants were calculated according to the law of mass action. In accordance with this law, the anion-exchange equilibrium can be written in general form as

$$n\mathbf{R}_{m}\mathbf{A}\mathbf{n}_{1} + m\mathbf{A}\mathbf{n}_{2}^{n-} \leftrightarrow m\mathbf{R}_{n}An_{2} + n\mathbf{A}\mathbf{n}_{1}^{m-}.$$
 (3)

The apparent constant of this equilibrium $(K'_{1,2}, L/mol)$ is then

$$\frac{(X_{\rm An_2})^m}{(X_{\rm An_1})^n} = K'_{1,2} \frac{(c_{\rm An_2^{n-}})^m}{(c_{\rm An_1^{m^-}})^n},\tag{4}$$

where X_{An_1} and X_{An_2} are molar fraction of ions An₁ and An₂ in the ionite phase; c_{An_1} and c_{An_2} are general analytical molar concentrations of these ions in solution; and *n* and *m* are the ion charges.

As follows from Eq. (4), the equilibrium ratio of ions concentrations in the solid phase is a linear function of the corresponding ratio in the liquid phase (including charges of the ions). The graphic representation of this dependence (the ratio of concentrations in solution on the x axis and the y axis in the ionite) is a linear sorption isotherm. The apparent ionexchange equilibrium constant is equal to the tangent of this line slope on the x axis.

The basicity of functional groups of anionite expressed in terms of $\overline{pK_b}$ was found by potentiometric titration. This value was calculated using the Henderson–Hasselbach equation [9]:

$$p\overline{K_b} = pH - m\log\left(\frac{\alpha}{1-\alpha}\right),\tag{5}$$

where α is the degree of anionite functional groups ionization, i.e., the ratio of the number of protons that transition to the ionite phase to the initial number of protons in the solution; and *m* is the tangent of the slope of the line.

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

The IR spectra of the sorbents were recorded using a Vector 22 Bruker Fourier transform infrared spectrometer. Dried samples of the ionites were ground in an agate mortar, then pressed into disks with spectrally pure KBr. Samples of the anionite were constant (6.5 mg of sorbent for every 1000 mg of KBr). Each spectrum was obtained as a result of 100 scans in the range of 400–4000 cm⁻¹.

RESULTS AND DISCUSSION

Ionic states of platinum metals in hydrochloric acid solutions were studied in detail in [12–14]. It was established that they depend on the acidity and temperature. Different transformations of the complexes (i.e., aquatation, hydrolysis, polymerization, isomerization) are characteristic for the studied systems. These processes are associated with so-called aging of noble metals solutions, which takes place when acid solutions are seasoned for more than 24 h. The aging of solutions leads to the formation of kinetically inert forms of complexes.

Existence of platinum chlorocomplexes in hydrochloric acid solutions is equally probable for the 2+ oxidation state and the 4+oxidation state. This is due to the proximity of the values of standard redox potentials in the $[PtCl_6]^{2-}/[PtCl_4]^{2-}$ ($E^0 = +0.726$ V) and $[PtCl_4]^{2-}/Pt$ ($E^0 = +0.780$ V) systems [12].

Studies of the behavior of platinum(II) chlorocomplexes in solutions at 150–200°C in autoclave [12] showed that the disproportionation reaction can occur in weakly acidic and neutral media:

$$PtCl_4]^{2-} \rightarrow [PtCl_6]^{2-} + Pt^0.$$
(6)

Hexachloroplatinate $[PtCl_6]^{2-}$ ($c_{HCl} > 3 \text{ mol/L}$) is predominant in strongly acidic solutions. Upon an increase in the pH of these solutions, complexes of Pt(II) coexisting with the chloride complexes of Pt(IV)

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in different proportions are formed. In addition, with decreasing acidity of the solution hydration and hydrolysis occur, which leads to the formation of aquachloro- and aquahydrochlorocomplexes of different composition $[Pt(H_2O)_nCl_{6-n}]^{n-2}$; $[Pt(H_2O)_k(OH)_mCl_{6-m-k}]^{k-2}$; $[Pt(OH)_mCl_{6-m}]^{2-}$; the formation of dinuclear complexes $[Pt_2Cl(OH)_7(H_2O)_2]$ [8, 15, 16] occurs as well, where n = 1, 2; m = 1-6; k = 1, 2.

Hexachlororhodiate $[RhCl_6]^{3-}$ predominates in solutions with a hydrochloric acid concentration of 6 mol/L. With declining acidity, the formation of aquachlorocomplexes of rhodium(III) $[RhCl_n(H_2O)_{6-n}]^{3-n}$, where 0 < n < 6, and *cis*- and *trans*-isomers of $[Rh(H_2O)_2Cl_4]^-$ and $[Rh(H_2O)_4Cl_2]^+$ occur. Polymerization causes the formation of dinuclear $[Rh_2Cl_9]^{3-}$ complexes [12, 15].

The dominant forms of platinum and rhodium in the studied systems are thus the complexes $[PtCl_6]^{2-}$ and $[RhCl_6]^{3-}$ (in 2 M HCl solutions), while in weakly acidic solutions, $[Pt(OH)Cl_5]^{2-}$, $[Pt(OH)_6]^{2-}$, $[Rh(H_2O)_2Cl_4]^-$ complexes are also formed. The formation of neutral and cationic forms of chlorocomplexes of rhodium $[Rh(H_2O)_3Cl_3]^0$, $[Rh(H_2O)_4Cl_2]^+$, and $[Rh(H_2O)_5Cl]^{2+}$ is also likely [12, 15, 16].

We recorded electronic absorption spectra of a freshly prepared solution of platinum and rhodium in the presence of 0.01 M HCl, and recorded them again after keeping the solution for three months. The resulting absorption spectrum of a freshly prepared hydrochloric acid solution of platinum(II, IV) and rhodium(III) has absorption maxima at wavelengths of 218 and 251 nm, which agrees with the published data [12]. The absorption maximum at 218 nm corresponds to the predominance of complex [PtCl₄]^{2–} and *cis–* and *trans–*complexes of [Rh(H₂O)₄Cl₂]⁺ and [Rh(H₂O)₂Cl₄][–] in the solution. The absorption maximum at 251 nm corresponds to the hexachlorocomplexes of platinum(II and IV) and rhodium(III) [12].

After keeping the solution for three months, both absorption maxima shifted to 198 and 261 nm, respectively, with declining intensity. This is indicative of the formation of such metal complexes as $[Pt(OH)Cl_5]^{2-}$ (260 nm), $[PtCl_6]^{2-}$, $[RhCl_5(OH)_5]^{3-}$ (261 nm), $[Pt(OH)_6]^{2-}$ (198 nm), and $[Rh(H_2O)_3Cl_3]^0$ (198 nm) in solution due to aging [12, 17].

Using the sorption concentration from platinum metal experiments, it was found that all of the studied ionites extract platinum from chloride solutions at levels of more than 85%. These sorbents extract rhodium considerably worse (>50%), except for the Purolite S 985 anionite (>90%). The degree of extraction of noble metals increases with decreasing acidity of the medium for all sorbents. For medium basic AM-2B anionite and the complexing polyamine Purolite S 985, this is due to the deprotonation of the nitrogen atoms of their functional groups, which leads to an increase in complex-forming ability of these sorbents.

In the case of strongly basic ionite Purolite A 500, the reduced noble metal extraction in highly acidic media is apparently due to competition between the complex anions of rhodium and platinum and chloride ions in the process of ion exchange. In addition, the lower extraction of rhodium(III) relative to platinum(II, IV) can be attributed to the greater kinetic inertness of its chloride complexes, especially in slightly acidic media, due to the presence of neutral and charged aquacomplexes $[Rh(H_2O)_3Cl_3]^0$, $[Rh(H_2O)_2Cl_4]^-$, $[Rh(H_2O)Cl_5]^{2-}$ [12].

It was also established that sorption characteristics of ionites with respect to Pt and Rh after seasoning solutions for three months deteriorate; this can be attributed to the aging of solutions, i.e., to the formation of kinetically inert hydroxo- and aqua complexes of rhodium and platinum that are sorbed with difficulty.

Sorption isotherms of the studied anionites were recorded; they are shown in Fig. 1 with AM-2B anionite as example. The curves for the sorption of platinum in the presence of rhodium are convex in nature (Fig. 1a), indicating the selectivity of ionites. Sorption isotherms of rhodium in the presence of platinum (Fig. 1b) have a pronounced linear region at the beginning of the process, which then goes into convex curves, indicating an increase in the selectivity of the process as sorption proceeds, i.e., as the degree of saturation of the anionites with extractable ions increases. It should be noted that these differences in the sorption isotherms are consistent with the selectivity of the studied ionites to the chloride complexes of platinum and rhodium. As mentioned above, the degree of affinity of the anionites for platinum(II, IV) ions is higher than for the ions of rhodium(III). This can be explained by the kinetic inertness of the rhodium chloride aqua- and hydroxocomplexes, and by the presence of neutral and cationic forms complexes rhodium in contacting solutions. For anionites Purolite S 985 and A 500, the sorption isotherm of platinum and rhodium have similar forms.

Further, the sorption isotherms of platinum in the presence of rhodium were brought to a linear form as in Eq. (2). Table 1 shows the parameters of the Langmuir equation, i.e., the maximum exchange capacity and apparent ion-exchange equilibrium constants, and correlation coefficients with straight isotherms, constructed in linear coordinates. As follows from the above data, the latter are close to unity, allowing us to consider the sorption isotherms of platinum in the presence of rhodium as a type of Langmuir isotherms.

For the case of the sorption isotherms of rhodium in the presence of platinum, the form of which does not correspond to the Langmuir isotherms, we calculated the apparent equilibrium constants according to the law of mass action (equation (4) and (5)). The results are shown in Table 2.

It is known [18] that the constants of ion exchange equilibria characterize the ion exchange affinity. Based



Fig. 1. Sorption isotherms: (a) Pt in the presence of Rh; (b) Rh in the presence of Pt from freshly prepared hydrochloric acid solutions on the AM-2B anionite: (*I*) 0.01 M HCl; (*2*) 2.0 M HCl; $c_{HCl} = 0.01$ M, $c_{Pt} = c_{Rh} = 0.5$ mmol/L.

on the values of apparent equilibrium constants in the studied system $\overline{\text{RCl}}$ -Pt(II, IV)-Rh(III)-HCl-H₂O, we may therefore conclude that ion exchange is selective, which is consistent with the above conclusion on the greater affinity of the studied ionites for platinum than for rhodium. In addition, the affinity of the studied ionites for extracted chlorocomplexes of platinum and rhodium increases with decreasing acidity of the contact solution (Tables 1 and 2).

We calculated the values of the dissociation constants of anionites acid-base functional groups pK_{h} according to Eq. (5), which were 2.9, 3.4, and 4.3 for the AM-2B, Purolite S 985, and A 500 anionites, respectively. However, no correlation of $p\overline{K}_b$ values with anionite selectivity was found. Despite the differences in the functional groups of the investigate anionites, the values of the exchange capacity of the noble metals and ion-exchange equilibrium constants seem very close to each other, if sorption is performed under identical conditions. Only in the case of extraction of rhodium in the presence of platinum in weakly acidic solutions is the equilibrium constant for Purolite S 985 more than three times higher than those for Purolite A 500 and AM-2B (Table 2). This effect is presumably due to deprotonation of the nitrogen atoms of polyamine functional groups of Purolite S 985, which increases its complexing ability. The basicity of the studied anionites is therefore not a decisive factor in the selectivity of the extraction of chloride complexes of platinum and rhodium in their copresence.

IR spectra and Raman spectra of these sorbents in the original chloride form and after saturation of their solutions of platinum metals were recorded to determine the mechanism of the sorption concentration of platinum and rhodium in their copresence on the selected anionites. They are shown in Figs. 2–4 with AM-2B anionite as an example.

The IR spectra of AM-2B anionite after saturation by individual solutions of rhodium and platinum, a peak appears at 451 cm⁻¹ (Fig. 2, spectra I-3), which corresponds to the presence of the complex anions of rhodium and platinum sorbed by anion exchange in the sorbent phase. However, the same peak corresponds to the vibrations of the bond of metal ions with electron-donating nitrogen atoms of the ionite, which, in its turn, indicates the complexation in the ionite phase [19].

The reduced intensity of the peak at 2855 cm^{-1} corresponds to the asymmetric and symmetric vibrations of the $-\text{NH}_3^+$ group of secondary amines salts [20]. The disappearance of the two major bands in the range of $2820-2750 \text{ cm}^{-1}$ and the appearance of several intense merged bands in the region of $2660-2460 \text{ cm}^{-1}$ (Fig. 2, spectra 1-3) is a consequence of stretching vibrations of $-\text{NH}^+$, $-\text{NH}_2^+$, $-\text{NH}_3^+$ groups [21]. The reduced intensity of the peak at 1510 cm⁻¹,

Table 1. Data on the correlation of the sorption isotherms of the platinum ions in the presence of rhodium ions from hydrochloric acid solutions with a linear dependence, and the parameters of the Langmuir equation

Sorbent	$c_{\rm HCl} = 2.0 \; {\rm mol/L}$			$c_{HCl} = 0.01 mol/L$		
	OE_{∞} , mmol/g	K, L/mmol	R^2	OE_{∞} , mmol/g	K, L/mmol	R^2
Purolite A 500	0.33	2.05	0.962	0.41	6.25	0.991
Purolite S 985	0.45	1.71	0.992	0.36	6.33	0.983
AM-2B	0.67	1.36	0.970	0.38	8.12	0.993

$c_{\rm HCl} = 2.0 \text{ mol/L}$	$c_{\rm HCl} = 0.01 \text{ mol/L}$					
0.02	0.05					
0.46	0.51					
0.14	0.23					
	$c_{\rm HCl} = 2.0 \text{ mol/L}$ 0.02 0.46 0.14					

Table 2. Apparent ion-exchange equilibrium constants calculated according to the law of mass action for the sorption of rhodium in the presence of platinum

and the displacement of the peaks at 1455, 1420, and 1362 cm⁻¹ to 1475, 1453, and 1377 cm⁻¹, respectively (Fig. 2, spectra 1-3), corresponds to vibrations in amino groups, and, according to [9], indicates a complexing mechanism of Rh and Pt complex ion sorption. In the region of 1174–1030 cm⁻¹, the shift of all bands at approximately 30 cm⁻¹ to longer wavelengths is observed, which might correspond to conformational vibrations of the polymer chain [22]. There is a shift of the peak at 3402 to 3421 cm⁻¹, which characterizes the stretching vibrations of the hydrogen bonding of free water in the ionite [23].

The IR spectrum of AM-2B anionite after its saturation with a solution of platinum and rhodium is identical to the spectrum of the sorbent after saturation by the individual solutions of platinum group metals (Fig. 2, spectra 2-4), indicating the immutability of sorption mechanism in the transition from individual to mixed solutions.

Data obtained on the basis of the Raman spectra confirm the sorption mechanism of platinum metals in AM-2B ionite established by IR spectroscopy.

In the Raman spectra of Purolite A 500 anionite after saturation by an individual solution of platinum, the peaks appear at 311 and 342 cm⁻¹ (Fig. 3, spectra *1* and *3*). In the spectrum of the ionite saturated by the

solution of rhodium, changes in intensities are also observed in this area (Fig. 3, spectra 1 and 2). These changes correspond to the vibrations of the $[PtCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[RhCl_6]^{3-}$ anions in the ionite phase as a result of anion exchange (Fig. 3, spectra 1 and 3), respectively, and they correspond to the vibrations of the $N \rightarrow Me$ bonds in complexation in the ionite phase [24]. The intensities of bands in the region of 3100–2840 cm⁻¹ increase considerably, which corresponds to the stretching vibrations of the hydrogen bond in the free water in the anionite phase [9]. The new bands at 1230-950 cm⁻¹ correspond to the oscillations of the functional amino groups in the ionite [9]. The intensity of the bands at $900-700 \text{ cm}^{-1}$ also increases, which characterizes the conformational changes of the polymer chain [9]. The increase in the intensity of peaks at 1611 and 1451 cm⁻¹ and appearance of the peak at 1573 cm⁻¹ characterizes the vibrations of amino groups in the anionite [21]. The bands appearing in the region of 1400–1320 cm⁻¹ are associated with the stretching vibrations of C-N bonds in the tertiary amines [21]. The spectrum of this anionite saturated by the solution of rhodium and platinum (Fig. 3, spectrum 4) with simultaneous presence undergoes the same changes as in the case of individual solutions.

From a comparison of the Raman spectra of Purolite S 985 anionite in its original form and after saturation of the individual solutions of rhodium and platinum (Fig. 4, spectra 1–3), we can see that the bands in the regions of 380–300 cm⁻¹ and 340–270 cm⁻¹, respectively, appear in the spectra. These are associated to vibrations of the N \rightarrow Me bonds that correspond to complexation in the ionite phase. In addition, these bands characterize the vibrations of the [RhCl₆]^{3–}, [PtCl₄]^{2–}, and [PtCl₆]^{2–} anions absorbed in anion exchange in the ionite phase [24]. The spectrum



Fig. 2. Fragments of the IR spectra of the AM-2B anionite saturated by platinum and rhodium chloride complexes: (1) in the original chloride form; (2) saturated solution of Rh; (3) saturated solution of Pt; (4) saturated solution of Pt and Rh. $c_{\text{HCl}} = 6.0 \text{ M}$, $c_{\text{Pt}} = c_{\text{Rh}} = 5.0 \text{ mmol/L}$.



Fig. 3. Fragments of the Raman spectra of Purolite A 500 anionite saturated by platinum and rhodium chloride complexes; for designations, see Fig. 2. $c_{HCl} = 1.0 \text{ M}$, $c_{Pt} = c_{Rh} = 5.0 \text{ mmol/L}$.



Fig. 4. Fragments of the Raman spectra of Purolite S 985 anionite saturated by platinum and rhodium chloride complexes; for designations, see Fig. 2. $c_{HCl} = 1.0 \text{ M}$, $c_{Pt} = c_{Rh} = 5.0 \text{ mmol/L}$.

of the sorbent saturated by a solution of rhodium and platinum (Fig. 4, spectrum 4) in copresence changes in the same areas as in the case of individual solutions.

Based on our results, the mixed sorption mechanism of chloride complexes of platinum(II, IV) and rhodium(III) on the investigated anionites that operates according to an anion exchange mechanism and complexation was thus established:

$$n\overline{\mathrm{RCl}} + [\mathrm{MeCl}_n]^{m^-} = \overline{\mathrm{R}_m[\mathrm{MeCl}_n]} + m\mathrm{Cl}^-, \qquad (7)$$

$$RN + [MeL_n] \Leftrightarrow [RNMeL_{n-1}] + L, \qquad (8)$$

where Me = Pt (Rh), L = Cl⁻, n = 4, 6 (for Pt) and 6 (for Rh), m = 2 (for Pt) and 3 (for Rh).

The established mechanisms are confirmed by data on the sorption extraction of rhodium and platinum ions, depending on the acidity of the solution. An increase is observed in the degree of extraction of noble metals from 89 to 99% for all anions when the concentration of hydrochloric acid falls from 2 to 0.01 M because with reduced solution acidity, when there is a deprotonation of functional groups, except for the anion exchange between the platinum, rhodium, and nitrogen atoms of functional groups, additional complexation occurs. In a strongly acidic medium ($c_{\rm HCl} = 2 \text{ mol/L}$) where the functional groups are fully protonated, these anionites adsorb chloride

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complexes of platinum(II, IV) and rhodium(III) by the ion-exchange mechanism only.

The obtained data on the sorption of platinum and rhodium allow us to recommend the studied anionites for introduction into the technological schemes of extraction of these metals from industrial solutions.

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