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Kinetics of Simultaneous Recovery of Platinum (II,IV) and Rhodium (III) from Sulfate-Chloride Solutions on some Anion Exchangers

Alexey M. Melnikov and Olga N. Kononova*

Siberian Federal University
79 Svobodny, Krasnoyarsk, 660041 Russia [1]

The paper is devoted to the kinetics of sorption concentration of platinum (II,IV) and rhodium (III) in their simultaneous presence in freshly prepared or stored sulfate-chloride solutions on some macroporous anion exchangers with different chemical structure.
It was shown that the process rate is high, although it is slightly reduced in case of stored solutions. The rate of platinum sorption concentration in the presence of rhodium on investigated resins is higher than of rhodium in the presence of platinum. The sorption process was controlled by gel diffusion for all the anion exchangers studied.

Keywords: platinum, rhodium, sorption, kinetics of sorption.

Introduction

To date, the growing demand for platinum group metals (PGM) stipulated their intensive mining and expansion of supplies of secondary raw materials (spent automobile catalysts, catalysts from chemical industry, electronic scrap and wastes of ore-dressing plants on noble metal-containing deposits). Low concentrations of PGM in solutions obtained after breakdown of such raw materials cause the application of sorption methods, known not only for their efficiency and selectivity, but also for environmental safety [1,2]. The successful industrial application of ion exchangers requires not only investigating their sorption properties, but also their kinetic behavior, as the satisfactory rate is one of the essential factors for resins' technological use.

The recovery of PGM from products of processing of secondary raw materials occurs often by means of sulfuric acid and sulfate solutions. In these solutions, platinum and rhodium exist in the form of sulfate complexes, which are more kinetically inert, compared to corresponding chloride complexes, especially of rhodium [1,3]. The sulfate complexes of platinum and rhodium are hardly sorbed and,

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* Corresponding author E-mail address: cm2@bk.ru

therefore, the sulfate solutions of PGM are needed to be activated before the sorption. Basically, the dopes of sodium chloride or autoclave-cured chlorination are used for this purpose [4-7]. However, the addition of hydrochloric acid to sulfate solutions of PGM facilitates the activation of these solutions without any additional expenses. The investigations [1,6,8] have shown that the sulfate complexes of PGM are absent in these systems. Based on that, we considered the recovery of platinum and rhodium from sulfate-chloride solutions as an important matter of scientific and practical interest.

Our previous investigations [6,8] were focused on rhodium recovery from sulfate-chloride systems, however, we did not covered the kinetics of its recovery in the presence of platinum. The present work is devoted to investigation of kinetics of simultaneous sorption concentration of platinum and rhodium from sulfate-chloride solutions on anion exchangers with different chemical structure.

Experimental

For the purpose of investigation, we selected several anion exchangers: AM-2B (Russia), Purolite S 985 and A 500 (Purolite Ltd, U.K.). These sorbents revealed the best sorption properties to PGM in our previous investigations [8,9]. The functional groups of Purolite A 500 are quaternary ammonia base (QAB), Purolite S 985 contains the polyamine groups, whereas the functionality of AM-2B is based on tertiary amino groups (~ 75 %) and of QAB (~ 25 %). The anion exchangers AM-2B and Purolite A 500 are synthesized on the basis of styrene and divinylbenzene (DVB). Purolite S 985 possesses the matrix on the basis of polyacrylate and DVB.

The initial rhodium stock solution with concentration 9.709 mmol/L in 6 M HCl was prepared by sintering of metallic rhodium quantity (0.25 g) with 5-fold excess (in mass) of BaO_2 [3]. The content of rhodium in the solution obtained was determined by a gravimetric method using sulfuric acid and thiourea [3]. The initial platinum stock solution with concentration 9.669 mmol/L in 6 M HCl was prepared by dissolution of accurately weighed quantity of H_2PtCl_6 in concentrated hydrochloric acid [3].

The sulfate-chloride solution was prepared by addition of sulfuric acid to chloride solution of platinum and rhodium. The initial concentrations of HCl and H_2SO_4 in the solutions obtained were equal to each other.

Before use, anion exchangers were prepared according to standard methods [10] and loaded with 1 M $NaCl$ aiming to convert the resins into the chloride form.

The sorption of noble metals was carried out from sulfate-chloride solutions with different acids concentrations (0.01 – 2.0 mol/L). The ratio of hydrochloric and sulfuric acids was 1 : 1. The initial concentration of platinum and rhodium in these solutions was 0.25 mmol/L.

The kinetic behavior of anion exchangers towards platinum and rhodium was investigated as follows. The resin quantities (0.1 g) were mixed with 10.0 mL of Pt/Rh chloride or sulfate-chloride solution, and then the suspensions were intensively stirred at > 800 rev/min. The saturation times were 0.5; 1; 2; 3; 5; 15; 30; 45; 60; 180; 360 and 1440 min. After a certain time period, the resins were quickly filtered off and the concentrations of noble metals in solution were determined spectrophotometrically with tin (II) chloride and potassium iodide [3]. Using the results obtained, the degree of saturation (F) of the resins as well as the process rate (v in mmol/g·s) were calculated as follows:

$$F = \frac{Q_t}{Q_\infty},$$
(1)

$$v = \frac{a_i}{t_i}, \qquad (2)$$

where Q_t and Q_∞ are the amounts (in mmol) of platinum or rhodium sorbed to time t and at equilibrium, respectively; a_i is quantity (in mmol) of platinum or rhodium sorbed to time t_i (in s) per 1 g of the resin.

Then the kinetic curves were plotted on the coordinates $F = f(t)$ and $v = f(t)$. After that, the half-exchange times ($t_{1/2}$, in s) were determined at $F = 0.5$.

The interpretation of results on kinetics was carried out using the Boyd-Adams' method [11-13], according to which the formal kinetic coefficient (B) was calculated from:

$$B = \frac{(1.06)^2 \cdot F^2}{t}. \qquad (3)$$

If the process is controlled by gel diffusion, the function $Bt = f(t)$ should be linear. The diffusion coefficients (D, in cm²/s) were calculated according to the equation:

$$D = \frac{r^2}{4\pi^2 \cdot t_{1/2}}, \qquad (4)$$

where r is radius of resin grain (in cm).

The results obtained in the present work were subjected to statistical processing according to conventional procedures [14,15]. The average experimental error was less than 5 %.

Results and discussion

It is known [1,3] that sulfate solutions contain the varied ionic forms of platinum and rhodium. There are very stable polymeric aquahydroxo-complexes as well as polynuclear aquahydroxo-sulfates, such as $[Pt_2(H_2O)_2(SO_4)_4]^{2-}$, $[Rh(H_2O)_2(SO_4)_2]^-$, $[Rh(OH)(H_2O)(SO_4)_2]^{2-}$ etc.

The presence of PGM sulfate complexes in solution causes the pronounced complication during recovery of these metals, given that the majority of analytical methods for noble metals separation are developed for chloride systems. They cannot be used for sulfuric acid media, because the kinetic inertness of PGM sulfate complexes is higher than inertness of chloride ones. For this reason, these solutions should be activated by adding sodium chloride or by autoclave-cured chlorination. However, now it is found that sulfate-chloride solutions supersede the activation of sulfate solutions, and besides, this process is rather easy [4-8].

Based on the electron absorption spectra of initial Pt/Rh sulfate-chloride solutions and on the data from reference [1], we have determined that both freshly prepared solutions and solutions stored over 3 months do not contain sulfate complexes of these metals. The chloride complexes, such as $[PtCl_6]^{2-}$, $[RhCl_6]^{3-}$, $[Pt(OH)Cl_5]^{2-}$, $[Pt(OH)_6]^{2-}$, $[Rh(H_2O)_2Cl_4]^-$ etc., are present in the system. During a storage of these solutions, the aquachloro- and hydroxocomplexes of platinum and rhodium, for example, $[Pt(H_2O)_nCl_{6-n}]^{n-2}$, $[Pt(OH)_nCl_{6-n}]^{2-}$, $[Rh(OH)_nCl_{6-n}]^{n-3}$, $[Rh(H_2O)_nCl_{6-n}]^{n-3}$, where $n = 1-6$, arrive in these media as a result of hydrolysis and aquation (the so-called "ageing" processes) [1].

We have studied in our previous work [9] the ion exchange equilibria and kinetics of simultaneous sorption concentration of platinum (II,IV) and rhodium (III) from freshly prepared and stored chloride solutions on some anion exchangers. We have determined that the resins possessed good kinetic

properties and the ion exchange was limited by gel diffusion. The isotherms of sorption of noble metals from sulfate-chloride solutions are similar to the isotherms of Pt/Rh sorption from chloride systems, proving the selectivity of the used resins.

The data on kinetic investigation of platinum and rhodium sorption from sulfate-chloride freshly prepared solutions on example of anion exchanger Purolite A 500 are presented in Fig. 1. The kinetic dependencies for the other resins are similar to these curves. It can be seen from these data that the anion exchanger studied possess good kinetic properties, since the process rate is high. For instance, over a period of 20 min, the resins are saturated on average with platinum complexes to 69 – 79 % and with rhodium ions to 57 – 76 % from their total exchange capacity. For comparison, these resins are saturated in 20 min to 53 – 80 % and 38 – 77 % with platinum and rhodium, respectively, while their sorption proceeds from chloride media.
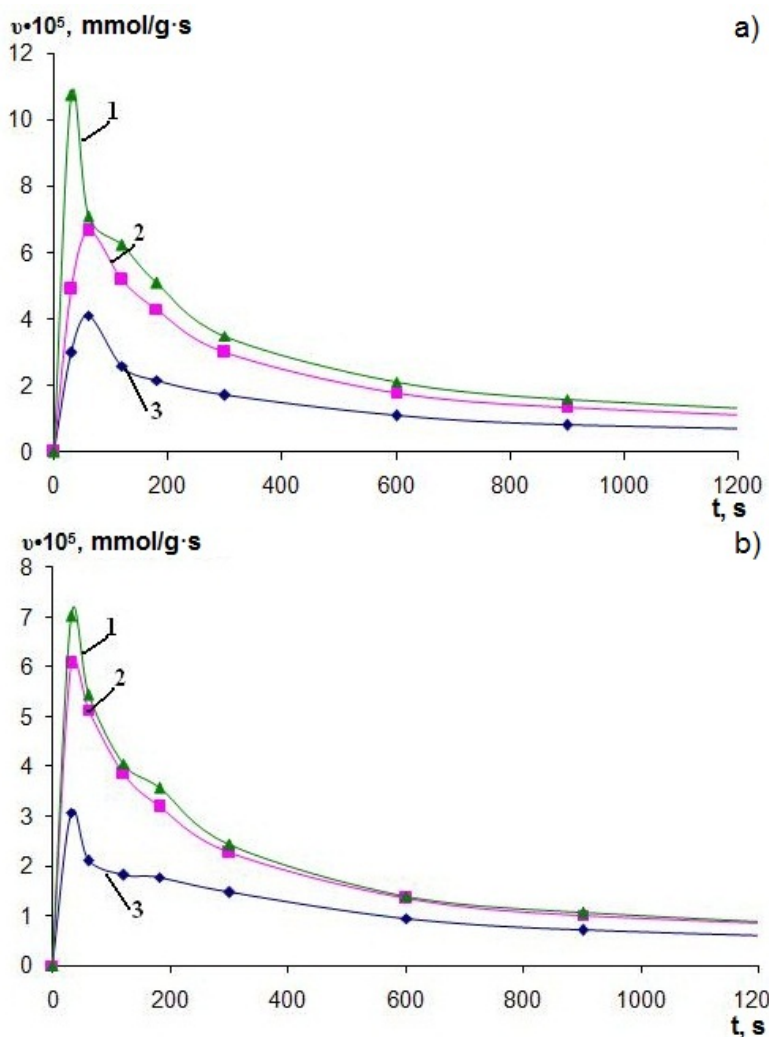

Fig. 1. Kinetic dependences of rates of sorption concentration of platinum in the presence of rhodium (a) and of rhodium in the presence of platinum (b) on anion exchanger Purolite A 500 from freshly prepared sulfate-chloride solutions with different acidity 1 – 0.01 M HCl/H_2SO_4; 2 – 0.1 M HCl/H_2SO_4; 3 – 2.0 M HCl/H_2SO_4 $(C(Pt)=C(Rh))=0.25$ mmol/L)

The rate of sorption concentration in weak acid solutions is higher than in strong acid ones. Such behavior of strong basic anion exchanger Purolite A 500 can be explained by competition between complex anions of rhodium and platinum and chloride ions during ion exchange process. Correspondingly, the lesser the concentration of Cl^- - ions is in solution, the weaker is their competing effect. As a result, an increase in Pt/Rh sorption is observed.

As for the weak basic resin Purolite S 985 and intermediate anion exchanger AM-2B, they behave similarly, i.e. their sorption ability towards Pt/Rh complexes grows with the decrease in acidity of contacting solution. This effect can be explained by the increase in deprotonation of the nitrogen atom in functional amine group, which increases the complexation ability of these sorbents [16].

It should be also noted that the recovery of platinum and rhodium from strong acid solutions proceeds with high process rate. The lower rate of rhodium (III) sorption in the presence of platinum (II,IV) can be explained by higher kinetic inertness of its chloride complexes, especially in weak acid solutions. It is known [1,3] that the neutral and charged aqua complexes $[Rh(H_2O)_3Cl_3]^0$, $[Rh(H_2O)_2Cl_4]^-$, $[Rh(H_2O)Cl_5]^{2-}$ are present in such solutions.

The study on kinetics of Pt/Rh sorption from stored sulfate-chloride solutions is of special interest, because these solutions are often used in the industry during PGM recovery. The data obtained (Table 1) show that the rate of sorption from solutions, stored over 3 months, decreases in comparison with freshly prepared ones. This can be explained by formation of kinetically inert hydroxo- and aqua complexes of platinum and rhodium. However, on the whole, the rate of Pt/Rh recovery from stored solutions remains on a high level. Thus, over of 20 min, the anion exchangers investigated are saturated from their total exchange capacity on the average to 51 – 60 % and to 35 – 46 % by platinum and rhodium, respectively. These values correlate with the results, which we have obtained earlier for chloride stored solutions (45 – 59 % and 34 – 55 % for Pt and Rh, respectively).

It can be seen from the data presented in Table 1 that the sorption concentration process proceeds with the rate of order of 10^{-5} mmol/g·s. The half-exchange time in the case of Pt recovery is much shorter than for Rh sorption. Therefore, the kinetic parameters are in agreement with our insight into the selectivity of investigated anion exchangers.

It can be also seen from Table 1 that the complexing sorbent Purolite S 985 reveals the best kinetic properties among the studied resins, owing to its ability for simultaneous ion exchange and complex formation in weak acidic media.

With the storage of Pt/Rh solutions, the sorption rate decreases, the half-exchange time is longer than in case of freshly prepared solutions. We consider it takes place because of formation of kinetically inert complexes of noble metals.

It should be noted that sorption of platinum and rhodium from stored sulfate-chloride solutions proceeds with higher rate than the recovery of these metals from stored chloride media, whereas in freshly prepared systems the rates of these processes are almost equal. Probably this phenomenon can be explained by lesser exposure to hydrolysis in sulfate-chloride solutions than in chloride systems.

The kinetics type during sorption concentration of platinum and rhodium from freshly prepared and stored sulfate-chloride solutions was determined using the classical Boyd-Adams' model with the corresponding criteria [11-13]. Fig.2 contains the dependencies $Bt = f(t)$ for anion exchanger Purolite A 500, which are consistent with the above-mentioned model for gel kinetics of ion exchange. These dependencies for the other sorbents investigated are also linear. Therefore, the Pt/Rh sorption

Table 1. Kinetic parameters of simultaneous sorption concentration of *Pt (II, IV)* and *Rh (III)* from freshly prepared and stored chloride and sulfate-chloride solutions ($C(Pt) = C(Rh)$ =0.25 mmol/L, $C(HCl) = C(H_2SO_4)$ =0.01 mol/L)

| Trade name	Kinetic parameters	Chloride solutions				Sulfate-chloride solutions			
		Freshly prepared		Stored		Freshly prepared		Stored	
		Rt	*Rh*	*Rt*	*Rh*	*Rt*	*Rh*	*Rt*	*Rh*
Purolite A 500	$t_{1/2}$, s	306	658	1270	1364	159	189	583	1055
	$D \cdot 10^8, cm^2/s$	5.18	2.41	1.25	1.16	9.97	8.38	2.72	1.50
	$v \cdot 10^5 \, mmol/g \cdot s$	2.80	1.23	0.72	0.54	5.07	3.66	1.08	0.81
Purolite S 985	$t_{1/2}$, s	174	182	572	639	157	185	289	945
	$D \cdot 10^8, cm^2/s$	9.11	8.71	2.77	2.48	10.09	8.57	5.48	1.68
	$v \cdot 10^5 \, mmol/g \cdot s$	6.41	3.76	1.63	1.34	7.31	3.92	2.28	1.11
AM-2B	$t_{1/2}$, s	307	488	1.62	1340	162	246	496	1264
	$D \cdot 10^8, cm^2/s$	13.21	8.31	3.21	3.03	14.09	9.28	8.18	3.21
	$v \cdot 10^5 \, mmol/g \cdot s$	2.98	2.02	0.74	0.59	5.46	2.99	1.32	0.78
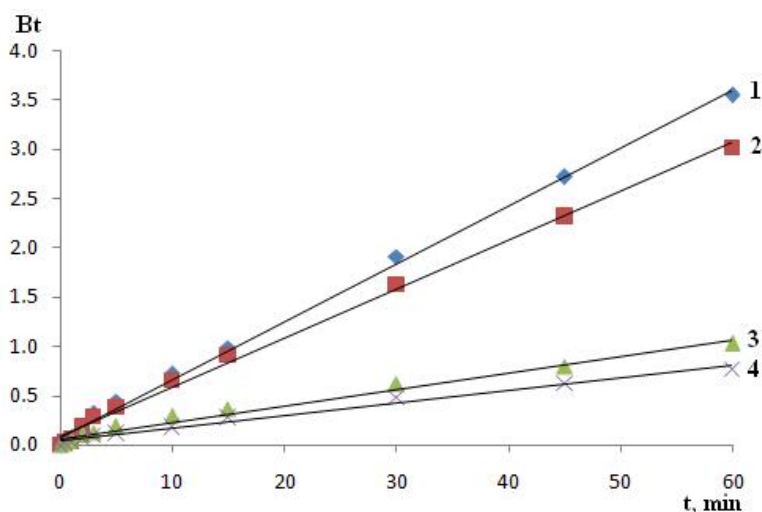
Fig. 2. Dependences of Bt function on time according to Boyd-Adams' model for gel diffusion kinetics of Pt / Rh sorption from sulfate-chloride solutions on anion exchanger Purolite A 500 1 – Pt in the presence of Rh (freshly prepared solution); 2 – Rh in the presence of Pt (freshly prepared solution); 3 – Pt in the presence of Rh (stored solution); 4 – Rh in the presence of Pt (stored solution) ($C(Pt) = C(Rh)$ =0.25 mmol/L; $C(HCl) = C(H_2SO_4)$ =0.01 mol/L)
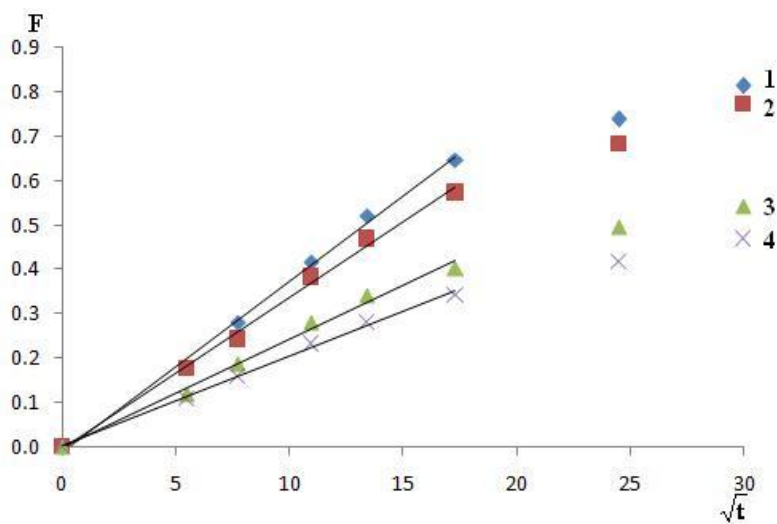

Fig.3. Dependences of saturation degree F on $\sqrt{t}$ during Pt / Rh sorption from sulfate-chloride solutions on anion exchanger Purolite A 500 1 – Pt in the presence of Rh (freshly prepared solution); 2 – Rh in the presence of Pt (freshly prepared solution); 3 – Pt in the presence of Rh (stored solution); 4 – Rh in the presence of Pt (stored solution) ($C(Pt) = C(Rh) = 0.25$ mmol/L; $C(HCl) = C(H_2SO_4) = 0.01$ mol/L)

is controlled by gel diffusion (i.e. inter-diffusion of ions exchanged in a resin bead). The dependencies $F = f(\sqrt{t})$ are also linear at small values of saturation degree F (Fig.3), and indicate the gel diffusion as well.

It should be noted that kinetics type during Pt / Rh sorption from sulfate-chloride freshly prepared and "aged" solutions on anion exchangers investigated is in agreement with gel kinetics during sorption of these metal complexes from chloride solutions, which we have studied in our previous work [9].

The main kinetic parameters of simultaneous Pt/Rh sorption are summarized in Table 1. The average diffusion coefficients are of the order of 10^{-8} cm²/s. Their values are higher for platinum sorption in the presence of rhodium, than for rhodium sorption in the presence of platinum under the same conditions. Such order of diffusion coefficients is in agreement with the data obtained for kinetics on selective ion exchangers [11,12,16].

Conclusions

The simultaneous sorption concentration of platinum (II,IV) and rhodium (III) from freshly prepared and stored sulfate-chloride solutions was investigated in dependence on initial concentrations of hydrochloric and sulfuric acids. The high rate of this process revealed in freshly prepared solutions, is decreased slightly in stored solutions. The rates of platinum sorption in presence of rhodium on the anion exchangers investigated are greater than the rates of rhodium sorption in presence of platinum under the same conditions. The whole ion exchange is controlled by gel diffusion for all the studied resins.

The results allow recommending the anion exchangers Purolite S 985 and A 500 as well as AM-2B for application in improved technological schemes for utilization of spent platinum-rhodium catalysts.

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Кинетика совместного извлечения платины (II,IV) и родия (III) из сульфатно-хлоридных растворов на некоторых анионитах

А.М. Мельников, О.Н. Кононова

Сибирский федеральный университет,
Россия 660041, Красноярск, пр. Свободный, 79

Изучена кинетика сорбционного концентрирования платины (II,IV) и родия (III) при совместном присутствии из свежеприготовленных и выдержанных сульфатно-хлоридных растворов некоторыми макропористыми анионитами различной химической структуры. Показана высокая скорость протекания этого процесса, которая несколько снижается при выдерживании растворов. Скорость сорбционного концентрирования платины в присутствии родия на исследуемых сорбентах превышает таковую для родия в присутствии платины. Сорбционный процесс контролируется гелевой диффузией для всех изученных анионитов.

Ключевые слова: платина, родий, сорбция, кинетика сорбции.