

## SORPTION OF PLATINUM METALS ON THE COPOLYMER GLYCIDYL METHACRYLATE-ETHYLENEDIMETHACRYLATE MODIFIED WITH ETHYLENEDIAMINE\*

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Sorption was investigated of the platinum metals rhodium, iridium, palladium and platinum from aqueous solutions of chloro complexes ( $\text{RhCl}_6^{3-}$ ,  $\text{IrCl}_6^{2-}$ ,  $\text{PdCl}_4^{2-}$ ,  $\text{PtCl}_4^{2-}$ ) on a chelating ion-exchanger prepared by reacting the macroporous copolymer glycidyl methacrylate-ethylenedimethacrylate with ethylenediamine. The dependence of the sorbed amount of ions on pH was determined, and the selectivity coefficients  $K_{\text{Rh}}^{\text{Ir}} = 10.8$  and  $K_{\text{Pt}}^{\text{Pd}} = 3.5$  were calculated. The elution of sorbed metals with hydrochloric acid of various concentration was also examined.

The separation of platinum metals still remains a difficult and open problem of the chemistry of precious metals. To solve the problem, great many methods of separation have been used, such as chromatography, extraction with the Soxhlet techniques, ion-exchange, *e.g.* a strongly basic anion exchanger used in the sorption of chloro complexes<sup>1</sup>.

This work is a study of the sorption and desorption of platinum metals by means of a chelating ion exchanger — the macroporous copolymer glycidyl methacrylate-ethylenedimethacrylate (*I*) reacted with ethylenediamine, which exhibits a high reactivity, mainly towards the transition metals<sup>2-4</sup>. The chelating character of this sorbent, which contains bound ethylenediamine as the analytically active group, was confirmed<sup>5</sup>, its selectivity with respect to the individual transition metals was ascertained, and the possibilities of separation of some mixtures of ions of these elements were indicated<sup>6</sup>. The results obtained offer good prospects for the application of the sorbent in the separation of platinum metals.

### EXPERIMENTAL

The macroporous copolymer *I* prepared by the suspension radical polymerization<sup>7</sup> of a mixture containing 60% (m/m) of glycidyl methacrylate and reacted with ethylenediamine was used

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as sorbent<sup>8</sup>. The nitrogen content in the dry sorbent (dried at 50°C to constant weight) was 2.61 mmol/g, particle size 125–150 µm, and 4.69 mmol/g in another sample with spherical particles, size 200–300 µm. The sorbent does not swell in aqueous solutions.

The preparation of the rhodium complex  $\text{Na}_3\text{RhCl}_6$  started from  $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  (cf.<sup>9</sup>); the solution of palladium ions and of  $\text{PdCl}_4^{2-}$  was prepared from a 10% solution of  $\text{PdCl}_2$ , and the solution of the complex anions  $\text{PtCl}_4^{2-}$  was obtained by diluting a solution of  $\text{H}_2\text{PtCl}_4$ , which was prepared from chloroplatinic acid by dissolving the latter in water and reducing the solution with sulphur dioxide<sup>10</sup>.  $\text{Na}_2\text{IrCl}_6$  was obtained by heating iridium metal and sodium chloride in a stream of chlorine<sup>11</sup>.

The determination of the dependence of metal sorption on pH was carried out using the batch method (0.2 g of dry sorbent, particle size 200–300 µm, ion concentration in solution 0.005M, pH adjusted with 3M-HCl or 3M-NaOH, total volume 100 ml, reaction time 60 min at 40 and 70°C). Desorption was investigated in a similar way and at the same temperatures (0.5 g of a sample with sorbed metal, 50 ml 4M-HCl, reaction time 3 h).

The selectivity coefficients were also measured in a static arrangement. To weighed samples containing 0.2 g of dry sorbent and 2.61 mmol N/g each, a solution of metal ions (50 ml) was added, and the mixtures were shaken for one hour. The total content of rhodium and iridium in the solutions before the reaction was 0.174 mmol, that of palladium and platinum was 0.261 mmol. The solutions were prepared so as to make the molar ratio of the two metals vary from 10:0 to 0:10. After the reaction had been completed and equilibrium had been established (60 min), the sorbent samples were filtered off, washed with 20 ml of water (5 ml each time), and the platinum metals present in the filtrate were determined by atomic absorption.

Sorption and elution at room temperature were followed by using the dynamic method (column, 9 mm inner diameter, 0.5 g of dry sorbent with 2.61 mmol N/g, flow rate 0.8 ml min<sup>-1</sup>).

The metal content in solution after sorption or elution was determined spectrophotometrically (Pt, Rh, Ir after reaction with tin(II) chloride<sup>12</sup>, Pd — with *p*-nitrosodimethylaniline<sup>13</sup>, Spektral spectral photometer manufactured by Carl Zeiss, Jena). Atomic absorption spectrometry (Varian-Techtron, AA6—BC6, Central Laboratories of the Institute of Chemical Technology) was used in the analysis of the ion mixtures.

## RESULTS AND DISCUSSION

The results obtained by measuring the dependence of the equilibrium amount of metal sorbed on pH of the solution used are summarized in Fig. 1. The lowest, almost imperceptible sorption is observed with rhodium. The highest sorption of all platinum metals investigated is found with palladium, at lower pH values. Iridium and platinum are sorbed roughly to the same degree: their amount gradually increases with increasing pH.

It was found that at the optimum pH, *i.e.* at pH of the maximum sorption, the following quantity of metals were bound from solution:

Ion	Rh(III)	Ir(IV)	Pd(II)	Pt(II)
Dry matter, mmol/g	0.11	1.15	1.75	1.20
pH <sub>optim</sub>	3.0	6.5	2.4	8.2

TABLE I

Sorption and Desorption of Platinum Metals on the Ethylenediamine Derivative of Copolymer I

Ion	Sorbed		Desorbed
	mmol/g	at pH	%
Rh(III)	0.113	2.2	0.9
Ir(IV)	0.790	3.4	12.7
Pd(II)	1.206	2.5	65.3
Pt(II)	0.590	6.3	24.4

Fig. 2 shows the dependence of the sorbed amount of platinum metals on the ion concentration in solution, which increased in the order  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$ M. The measurement was carried out under dynamic conditions. A solution of certain concentration was let to pass through the column until the state of equilibrium had been established. After 100 ml of solution (a volume sufficient for the establishment of equilibrium) had flowed through the column, the more concentrated solution was used.

Rhodium is sorbed quantitatively only during the flow of the first 30 ml of the  $10^{-4}$ M solution. Palladium is sorbed quantitatively from the whole volume with the exception of the last 70 ml of the  $10^{-2}$ M solution. Iridium is completely sorbed from the  $10^{-4}$ M solution, while complete sorption of platinum occurs already from the first 30 ml of the  $10^{-3}$ M solution (Fig. 2).

Fig. 3 summarizes results of the elution of bound metal ions on the sorbent with 4M, 8M and 12M-HCl. Each of the four platinum metals used was eluted from the

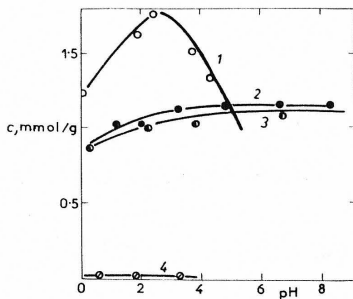


FIG. 1

Determination of the Sorption Capacity on pH for  $\text{PdCl}_4^{2-}$  (1),  $\text{IrCl}_6^{2-}$  (2),  $\text{PtCl}_4^{2-}$  (3),  $\text{RhCl}_6^{3-}$  (4)

0.2 g of dry sorbent, particle size 200 to 300  $\mu\text{m}$ , solution volume 100 ml, concentration 0.005M.

sorbent each time with 100 ml of HCl of the respective concentration. The desorption of metals with hydrochloric acid is low, in the case of rhodium virtually imperceptible (Table I). Even a considerable rise in the acid concentration has no essential impact on the amount of eluted ions, except Pd(II). Neither does elevated temperature affect the effectivity of elution of the ions of Pd(II), Rh(III), Ir(IV) with 4M-HCl. Only the platinum content decreased in this case, by 2.8% at 40°C and by another 1.4% at 70°C; 71.4% of sorbed metal remained bound. The elution of iridium could not even be raised by the reduction of the bound complex of Ir(IV) in the sorbent using 4% hydroxyl ammonium chloride before the elution with the acid<sup>1</sup>.

The dependence of the sorbed amount of metal on pH (Fig. 1) allows to separate some mixtures of these ions. The measure of selectivity of the sorbent towards various ions is given by the selectivity coefficient  $K_B^A$  defined by the equation

$$K_B^A = \frac{[A]_r^b [B]_s^a}{[B]_r^a [A]_s^b},$$

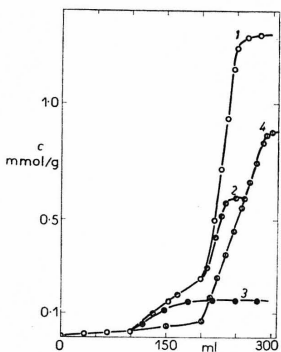


FIG. 2

Sorption of  $\text{PdCl}_4^{2-}$  (1),  $\text{PtCl}_4^{2-}$  (2),  $\text{RhCl}_6^{3-}$  (3),  $\text{IrCl}_6^{2-}$  (4) under Dynamic Conditions from Solutions of the Concentration  $10^{-4}\text{M}$  (0–100 ml),  $10^{-3}\text{M}$  (100–200 ml),  $10^{-2}\text{M}$  (200–300 ml)

In the range 0–100 ml all curves follow the course of the sorption of  $\text{PdCl}_4^{2-}$  (1). Column, inner diameter 9 mm, flow rate  $0.8 \text{ ml min}^{-1}$ , 0.5 g of dry sorbent, particle size 125–150  $\mu\text{m}$ .

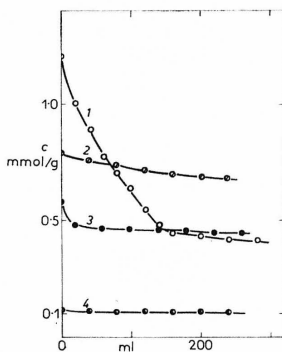


FIG. 3

Elution of the Pd(II) (1), Ir(IV) (2), Pt(II) (3), Rh(III) (4) Ions under Dynamic Conditions

Column, inner diameter 9 mm, flow rate  $0.8 \text{ ml min}^{-1}$ , 0–100 ml 4M-HCl, 100–200 ml 8M-HCl, 200–300 ml 12M-HCl.

where [A] and [B] respectively stand for the analytical concentration of the ions A and B having the numerical coefficients  $a$ ,  $b$  in the exchange equation; the subscripts  $r$  and  $s$  correspond to the sorbent and solution phases respectively.

Values summarized in Table II were used to calculate the average selectivity coefficient  $K_{Rh}^{Ir} = 10.8$ , which shows that the separation of the two ions from their mixed solution is real. On the other hand, the average value  $K_{Pt}^{Pd} = 3.5$  (Table III) shows that there is only a limited possibility of mutual separation of these ions on the sorbent used.

TABLE II

Selectivity Coefficient  $K_{Rh}^{Ir}$  of the Ethylenediamine Derivative of Copolymer I at pH  $\approx$  3.5

$\left(\frac{Ir(IV)}{Rh(III)}\right)^a$	Metal concentration at equilibrium				$K_{Rh}^{Ir}$
	polymer, mmol/g		solution, mmol/ml. $10^3$		
	Ir(IV)	Rh(III)	Ir(IV)	Rh(III)	
9	1.070	0.02	1.76	0.40	12.2
2.3	0.565	0.06	1.34	1.63	11.5
1	0.410	0.10	0.83	1.91	9.4
0.43	0.235	0.12	0.47	2.19	9.1
0.11	0.105	0.19	0.16	3.37	11.6

Starting molar ratio of metal ions in solution.

TABLE III

Selectivity Coefficient  $K_{Pt}^{Pd}$  of the Ethylenediamine Derivative of Copolymer I at pH  $\approx$  2.5

$\left(\frac{Pd(II)}{Pt(II)}\right)^a$	Metal concentration at equilibrium				$K_{Pt}^{Pd}$
	polymer, mmol/g		solution, mmol/ml. $10^3$		
	Pd(II)	Pt(II)	Pd(II)	Pt(II)	
9	0.915	0.106	0.522	0.149	3.45
2.3	0.750	0.305	0.329	0.477	3.57
1	0.627	0.351	0.272	0.548	3.58
0.43	0.384	0.458	0.255	0.912	3.04
0.11	0.130	0.689	0.049	0.974	3.80

<sup>a</sup> Starting molar ratio of metal ions in solution.

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