A STUDY TO THE ISOLATION OF IRIDIUM FROM PLATINUM METAL MIXTURES

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Sorption from solution onto a glycidyl methacrylate–ethylene dimethacrylate copolymer modified with ethylenediamine was employed for the isolation of platinum metals. The sorption selectivity coefficients for Rh(III), Ir(IV), Pt(IV) and Pd(II) chloro complexes were determined in the static mode and the values of $K_{Rh}^{Ir} = 10.9$, $K_{Ir}^{Pt} = 5.4$ and $K_{Ir}^{Pd} = 7.3$ were obtained. The dependence of the sorption capacity of the resin on pH of the sorption solution was established; the highest sorption capacity for palladium, 1.7 mmol g^{-1}, was found at pH 3. A procedure for the separation of iridium from palladium is suggested making use of the complexing ability of the sorbent. UV-VIS spectroscopic measurements revealed that Ir(IV) is reduced to Ir(III) on the sorbent and $[IrCl_6]^{3-}$ ions are formed. This reduction is caused by aquation of the hydrophilic particles of the sorbent with bonded $[IrCl_6]^{2-}$ anions.

The occurrence of platinum metals in common, along with their unique properties, has long been stimulating interest in methods for their mutual separation. From among the existing methods, ion exchange is popular owing to its relatively simple performance and, at the same time, high effectivity. Various ion exchange resins can be used for the isolation of iridium, whose separation remains a difficult task in the chemistry of precious metals.

The ion exchange method for the separation of iridium from platinum metals, elaborated particularly for binary mixtures[1,2], makes use of the differences in the electrostatic and kinetic behaviour of complexes and, in particular, of selective oxidation-reduction processes. The application of redox reagents such as $N_2H_5^+$, Fe^{2+}, Ce^{4+}, Cl_2, enabling iridium to be converted from one oxidation state [(Ir(III), Ir(IV)] to another (Ir(III), Ir(IV) and thereby isolated, is commonplace in ion exchange separation procedures[3-9].
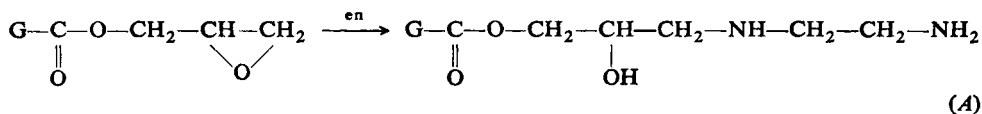
By contrast, we attempted to avoid the use of such reagents for the isolation of iridium. We used a glycidyl methacrylate resin containing ethylenediamine complexing groups with the aim to exploit all of its functions, in view of the fact that this resin can coordinate platinum metals and also, in the protonated form, bond anionic complex species of the metals by electrostatic interaction. Moreover, the sorbent can

exert a substantial effect on reactions as an efficient catalyst for oxidation-reduction processes[10]. This approach was also warranted by the fact that previously we made use of the combined chelating and ion exchanger properties of the sorbent for the separation of chloro complexes of Rh(III), Pt(IV) and Pd(II) (ref.[11]).

EXPERIMENTAL

Sorbent

The sorbent was a glycidyl methacrylate–ethylene dimethacrylate copolymer[12] modified with ethylenediamine according to the scheme,

$$G\!-\!\underset{\underset{\displaystyle O}{\|}}{C}\!-\!O\!-\!CH_2\!-\!\underset{\diagdown\!\underset{\displaystyle O}{\diagup}}{CH}\!-\!CH_2 \xrightarrow{\;en\;} G\!-\!\underset{\underset{\displaystyle O}{\|}}{C}\!-\!O\!-\!CH_2\!-\!\underset{\underset{\displaystyle OH}{|}}{CH}\!-\!CH_2\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!NH_2$$

$$(A)$$

where G is the polymeric matrix; the righ-hand modified gel will be denoted Gen throughout this paper.

The theoretical exchange capacity of this sorbent with $d_p = 0.05 - 0.10$ mm was calculated based on its nitrogen content; $Q_g(N) = 1.92$ mmol g^{-1}. The copolymer was prepared at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences in Prague.

Chemicals and Solutions

Solutions of palladium and rhodium chloro complexes in a concentration of 0.1 mol l^{-1}, chloroplatinic acid and iridium metal (Safina, Jesenice, Czechoslovakia) were used. Iridium powder was transferred to solution by chlorination at 600°C in a mixture with sodium chloride[13]. The concentration of hydrochloric acid in the stock solution of platinum metal chloro complexes with $c_{Me} = 0.01$ mol l^{-1} was 1.0 mol l^{-1}. The Na_3IrCl_6 complex was prepared by reduction of sodium chloroiridate(IV) with sodium nitrite[14] (calculated: 40·6% Ir, found: 40·9% Ir).

Analytical Methods

Samples containing the individual metals and their binary mixtures were analyzed photometrically with a Spekol 11 spectrophotometer (Carl Zeiss, Jena, G.D.R.). Palladium in the presence of iridium was determined after extraction of the Pd(II) complex with α-furildioxime into chloroform, iridium was determined in the aqueous phase after reaction with $SnCl_2$ (ref.[15]). Platinum in the presence of iridium was extracted as the iodide complex from 6M-HCl into a 15% solution of tributyl phosphate in hexane and after evaporating the organic phase, determined with *p*-nitrosodimethylaniline[15]; iridium in the aqueous phase was determined as above. Rhodium in the presence of iridium and multicomponent mixtures of platinum metals were analyzed by atomic absorption spectrometry using a Varian AA 775 instrument. Electronic reflection and absorption spectra of Ir(IV) and Ir(III) complexes were measured on a Perkin–Elmer 340 spectrophotometer. The pH was measured with an OP 204/1 pH-meter (Radelkis, Budapest, Hungary) fitted with a glass electrode and a calomel electrode.

Measurement of Selectivity Coefficients, Practical Sorption Capacities,
Sorption and Desorption

The selectivity coefficients were determined in the static mode at room temperature. Amounts of 0·2 g of dry sorbent were weighed into flasks, 50 ml volumes of solutions of platinum metals in hydrochloric acid were added and the whole was shaken for 3 h; thereafter, both the solution and the sorbent were analyzed for the metals. For this, the metal was released from the sorbent with a mineral acid, the sorbent was annealed gently and the ashing residue was dissolved in concentrated mineral acids for analysis.

The pH dependence of the practical sorption capacity of the resin for platinum metals was measured by the batch method. The amount of dry sorbent was 0·2 g, concentration of chloro complexes in solution 5 mmol l^{-1}, pH was adjusted with 3M-HCl or 5M-NaOH, the total volume was 100 ml, reaction time at 20°C was 60 min. The sorption and desorption of iridium and palladium was performed in the dynamic mode on a column of 1 g of dry sorbent 10 × 32 mm dimensions. Before use, the sorbent was converted to the Cl^- form with HCl and rinsed with distilled water to a neutral reaction. The sorption solution (10—400 ml) was fed at a flow rate of 0·8 ml min^{-1}, the chloro complex concentration was 4 to 10 mmol l^{-1} and pH 0 to 1. After rinsing the column with water, iridium was eluted with 1M to 3M-HNO$_3$, palladium with 5M-HCl. The freedom of the packing from platinum metals was verified by analysis after its ashing. The measurements were repeated 10 times. Typical data of the desorption of iridium and palladium from the sorbent are given in Table I.

RESULTS AND DISCUSSION

The exchange properties of Ir(IV), Rh(III), Pt(IV) and Pd(II) chloro complexes on the modified sorbent were evaluated in terms of the selectivity coefficients calculated as

$$K_A^B = ([GenB]^a [A]^b)/([GenA]^b [B]^a) \qquad (1)$$

with respect to the exchange of the A^{a-}, B^{b-} anions on the resin,

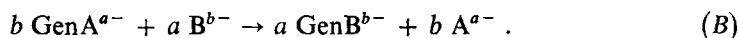$$b \, GenA^{a-} + a \, B^{b-} \rightarrow a \, GenB^{b-} + b \, A^{a-} . \qquad (B)$$

TABLE I
Separation of a mixture of Ir(IV) and Pd(II) (0·2 mmol Ir and 0·4 mmol Pd per g Gen sorbent)

Eluent	V ml	Desorbed, %	
		Ir	Pd
1M-HNO$_3$	20	31·5	0
2M-HNO$_3$	70	95·6	0
3M-HNO$_3$	10	100	0
5M-HCl	100	—	100

The a and b values are the absolute charges of the A and B ions, respectively, [A] and [B] are the analytical concentrations of the two ions in the solution (in mol l^{-1}) and [GenA] and [GenB] are the A and B ion contents of the sorbent (in mmol g^{-1}). The data are given in Tables II—IV.

In the conditions of static equilibrium $(c(HCl) = 1 \text{ mol } l^{-1})$, platinum metals in the sorbent–sorption solution of chloro complexes system exist predominantly in the form of the $[IrCl_6]^{2-}$, $[RhCl_6]^{3-}$, $[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$ anions, both in solution and, without change, in the sorbent phase. This is confirmed by the electronic absorption and reflection spectra[11,16]. The oxidation state remains unaltered also

TABLE II

Values of the selectivity coefficient K_{Rh}^{Ir} for $[IrCl_6]^{2-}$ and $[RhCl_6]^{3-}$ chloro complexes on Gen sorbent

$c_{Ir} : c_{Rh}$ ratio in starting solution[a]	Equilibrium concentration				K_{Rh}^{Ir}
	on sorbent, mmol g^{-1}		in solution, mol l^{-1}		
	Ir	Rh	Ir	Rh	
9 : 1	1·07	0·02	1·76	0·40	12·2
5 : 5	0·41	0·10	0·83	1·91	9·4
1 : 9	0·10	0·19	0·16	3·37	11·1

[a] $c_{Ir} + c_{Rh} = 3·48 \text{ mmol } l^{-1}$.

TABLE III

Values of the selectivity coefficient K_{Ir}^{Pt} for $[IrCl_6]^{2-}$ and $[PtCl_6]^{2-}$ chloro complexes on Gen sorbent

$c_{Ir} : c_{Pt}$ ratio in starting solution[a]	Equilibrium concentration				K_{Ir}^{Pt}
	on sorbent, mmol g^{-1}		in solution, mol l^{-1}		
	Ir	Pt	Ir	Pt	
9 : 1	0·41	0·06	0·37	0·01	5·4
5 : 5	0·30	0·25	0·14	0·02	5·8
1 : 9	0·04	0·44	· 0·09	0·19	5·2

[a] $c_{Ir} + c_{Pt} = 2·20 \text{ mmol } l^{-1}$.

for Ir in the $[IrCl_6]^{2-}$ anion bonded to the sorbent, after isolation of the latter from the solution. Therefore, selectivity coefficient calculations were invariably based on the reaction of Ir(IV) ions possessing the homogeneous coordination sphere $[IrCl_6]^{2-}$.

The average selectivity coefficients obtained are very low, viz. $K_{Rh}^{Ir} = 10 \cdot 9$, $K_{Ir}^{Pt} = 5 \cdot 4$, and $K_{Ir}^{Pd} = 7 \cdot 3$. If the separation of the chloro complexes only relied on the simple ion exchange, possibilities for the separation of platinum metals in these systems would be rather limited. Isolation of rhodium would be prospective, the $[RhCl_6]^{3-}$ complex having a low affinity for the sorbent. The sorption capacities of the resin in dependence on the pH of the sorption solution containing platinum metals (Table V) confirm that particularly at high acidity, the rhodium content of the sorbent phase is very low and only increases with increasing pH. This increase

TABLE IV

Values of the selectivity coefficient K_{Ir}^{Pd} for $[IrCl_6]^{2-}$ and $[PdCl_4]^{2-}$ chloro complexes on Gen sorbent

$c_{Ir} : c_{Pd}$ ratio in starting solution[a]	Equilibrium concentration				K_{Ir}^{Pd}
	on sorbent, mmol g^{-1}		in solution, mol l^{-1}		
	Ir	Pd	Ir	Pd	
9 : 1	0·28	0·06	0·72	0·02	7·7
5 : 5	0·17	0·24	0·37	0·07	7·4
1 : 9	0·03	0·42	0·09	0·18	7·0

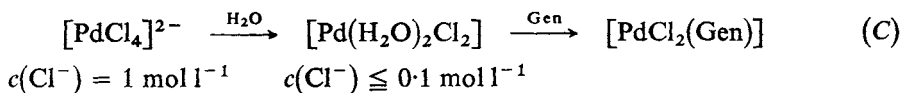[a] $c_{Ir} + c_{Pd} = 2 \cdot 16$ mmol l^{-1}.

Table V

Dependence of sorption capacity of Gen resin on pH of solution of platinum metals

pH	Q_g, mmol g^{-1}			
	Rh(III)	Ir(IV)	Pt(IV)	Pd(II)
0·5	0·1	1·0	1·2	1·2
1·5	0·2	1·0	1·2	1·5
3·0	0·4	0·9	1·1	1·7
4·0	0·9	0·8	0·9	1·6

can be explained in terms of changes in the bonding of Rh(III) to the sorption-active groups of the resin. As the acidity decreases, so does the amount of protonated amine groups G—H_2en^{2+}, and coordination of rhodium by the polymeric amine ligands, $[RhCl_4(Gen)]^-$, starts to prevail over the electrostatic interaction of the $[RhCl_6]^{3-}$ anions. The increasing sorption of palladium with increasing pH can be explained likewise[11]. The kinetically inert $[PtCl_6]^{2-}$ and $[IrCl_6]^{2-}$ chloro complexes remain bonded to the sorbent and no substitution reactions in the coordination spheres of the metals are observed; the practical sorption capacities remain nearly unaffected by pH changes.

The sorbent can be used for the separation of platinum metals if both its chelating ability and its anion exchanger function are employed. An example of this is the following procedure for the separation of iridium and palladium. The $[IrCl_6]^{2-}$ and $[PdCl_4]^{2-}$ complex ions are first sorbed from acid chloride solutions (pH < 2) where the sorbent in the Cl^- form plays the anion exchanger role. During the ensuing intensive washing of the sorbent (with the bonded iridium(IV) and palladium(II) chloro complexes) with water, the kinetically labile chloropalladate(II) anion undergoes the substitution reaction:

$$[PdCl_4]^{2-} \xrightarrow{\text{H}_2\text{O}} [Pd(H_2O)_2Cl_2] \xrightarrow{\text{Gen}} [PdCl_2(Gen)] \qquad (C)$$
$$c(Cl^-) = 1 \text{ mol } l^{-1} \qquad c(Cl^-) \leqq 0\cdot1 \text{ mol } l^{-1}$$

The amount of neutralized sorption-active groups decreases with decreasing concentration of hydrogen ions. Palladium then is bonded to N-donor atoms of the support giving rise to the thermodynamically stable *cis*-isomeric chelates[11].
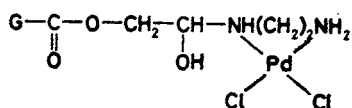
The next effect is a preferential elution of iridium (Table I), palladium being bonded strongly by the polymeric amine ligands; converted to the chloro complex, palladium is only desorbed by 5M-HCl:

$$[PdCl_2(Gen)] \xrightarrow{\text{HCl}} [PdCl_4]^{2-} + G\text{—}H_2en^{2+} \qquad (D)$$
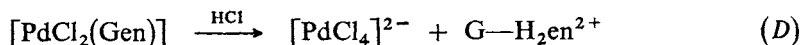
The gradual separation can be well monitored visually owing to the initially colourless sorbent acquiring the colour of the complexes bonded.

Attention was paid to the behaviour of the iridium(IV) chloro complexes in the conditions of sorption and elution; the reaction of the $[IrCl_6]^{2-}$ ions with the ethylenediamine functional groups of the sorbent and the complex formation were

studied by electronic (UV-VIS) reflection spectroscopy (Fig. 1). Iridium(IV) was found to be reduced at the sorbent even in the absence of a reductant; the existence of $[IrCl_6]^{3-}$ ions bonded to the resin after sorption of iridium from solution of the $[IrCl_6]^{2-}$ chloro complex was confirmed. The sorption solution of sodium chloroiridate(IV) in a concentration of 20 mmol l^{-1} in 1M-HCl exhibits bands at 270, 306, 340, 416, 435, 488 and 584 nm, characteristic of the $[IrCl_6]^{2-}$ anion which has been studied in detail[17,18]. The same spectrum was obtained for the sorption solution in equilibrium with the sorbent, giving evidence that the oxidation state of iridium and composition of the coordination sphere remained intact. Reduction of the $[IrCl_6]^{2-}$ anion bonded to the amine sorbent takes place only after isolation of the resin from the chloride medium. Iridium exists on the sorbent in the form of the $[IrCl_6]^{2-}$ anion also during the elution with 5M- to 1M-HCl.

The change in the oxidation state of iridium during the washing of the sorbent with water is accompanied by a colour change from the red-brown caused by the $[IrCl_6]^{2-}$ chloro complexes to a green colour typical of iridium(III) compounds. During the passage of water through the column, the concentration of hydrogen and chloride ions in the sorbent phase lowers, and transient aquated Ir(IV) chloro complexes are formed on the amine sorbent; these undergo instantaneous reduction under the catalytic action of the macroporous resin[19]. Transient participation of the hydroxy groups of the sorbent in the substitution of the chloride ligands in the Ir(IV) chloro complexes is not impossible.

Since the reduction of iridium(IV) on the sorbent is very fast, the interaction of the hydrophilic sorbent particles with water in the dynamic mode was not deliberately
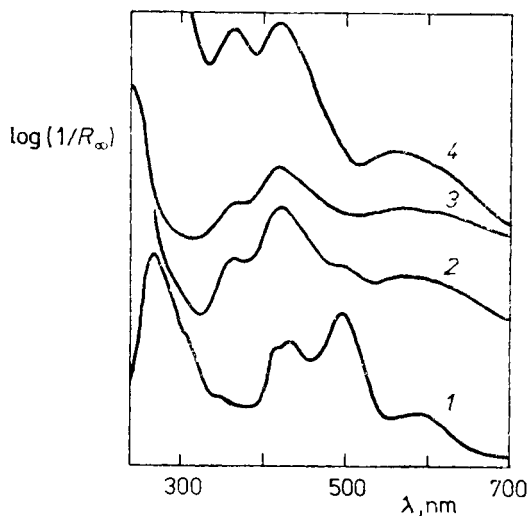

FIG. 1

Electronic reflection spectra of Ir(IV) and Ir(III) chloro complexes. Iridium $[IrCl_6]^{2-}$ bonded to sorbent from solution containing Na_2IrCl_6 in a concentration of 20 mmol l^{-1} in 1M-HCl. 1 $[IrCl_6]^{2-}$ on sorbent after washing with 1M-HCl, 2 $[IrCl_6]^{3-}$ with an unreduced fraction of $[IrCl_6]^{2-}$ on sorbent after washing with 0·1M-H_2SO_4, 3 $[IrCl_6]^{3-}$ on sorbent after washing with water, 4 crystalline Na_3IrCl_6

prolonged. The concentration of Cl^- ions remaining in the sorbent phase is still sufficient for a preferential formation of iridium(III) chloro complexes, which are kinetically inert. Only coordinated $[IrCl_6]^{3-}$ anions were identified on the sorbent; their spectrum consists of three bands at 360, 420 and 570 nm (Fig. 1), interpreted in detail in ref.[20].

By washing the sorbent containing the coordinated $[IrCl_6]^{3-}$ species with $2M$-H_2SO_4, eluate was obtained whose spectrum was typical of the chloroiridate(III) complex. Substitution by water in the coordination sphere of the $[IrCl_6]^{3-}$ anions bonded to the sorbent, giving rise to the $[Ir(H_2O)Cl_5]$ complexes, takes place during a longer aquation phase.

The fact that chloroiridate(III) ions are formed on the sorbent in the absence of an extra added reductant is of importance for the application of sorbents of this kind, with ethylenediamine sorption-active groups, to separations of mixtures of platinum metals.

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