



## Sorption of palladium(II) complexes onto the styrene–divinylbenzene anion exchange resins

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### ABSTRACT

The sorption behaviour of palladium(II) complexes onto the strongly basic styrene–divinylbenzene anion exchange resins of type 1 (Dowex MSA-1) and type 2 (Dowex MSA-2) from the chloride and chloride–nitrate solutions was investigated. The breakthrough curves of Pd(II) were determined and the mass and bed distribution coefficients, the working anion exchange capacities as well as the amount of palladium(II) complexes sorbed onto the anion exchangers under discussion were calculated. The effect of the phases contact time, hydrochloric and nitric acids and sodium chloride concentrations onto the sorption process was studied. The FT-IR spectra of pure anion exchangers and those loaded with palladium(II) complexes were recorded, too. The FT-IR spectra confirmed the difference in the composition of resin's functional groups and in Pd(II) binding additionally by means of O atoms involved in functional groups of Dowex MSA-2.

The highest working anion exchange capacity is observed in the 0.1 M HCl solution; 0.0616 and 0.0583 g/cm<sup>3</sup> for Dowex MSA-1 and Dowex MSA-2, respectively. Both anion exchange resins can be efficiently applied in sorption of Pd(II) complexes.

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### 1. Introduction

The separation and determination of trace amounts of precious metals in various samples (e.g. environmental samples) present two main problems such as: interferences of the sample matrix and low metal concentration. A preconcentration procedure is therefore often needed to increase concentration levels in the analysed solutions and remove matrix interferences. The most widely used techniques for the separation and preconcentration of trace noble metal ions include fire assay [1–3], coprecipitation [2–5], liquid–liquid extraction [4,6,7], ion exchange and sorption [7–9]. Strongly basic anion exchange resins of styrene and divinylbenzene skeleton find wide applications in the sample pretreatment for separation and concentration of the platinum group metals (PGMs). Styrene–divinylbenzene copolymers used as matrices for ion exchange resins possess many advantages e.g. excellent physical strength, resistance to the degradation by higher temperature or oxidation [10].

The goal of this paper was to study sorption behaviour of palladium(II) complexes onto the strongly basic, macroporous anion

exchange resins: Dowex MSA-1 (type 1) and Dowex MSA-2 (type 2) from the chloride (HCl; HCl–NaCl) and chloride–nitrate solutions (HCl–HNO<sub>3</sub>). A few conditions such as: the phases contact time, the macrocomponent addition (sodium chloride) as well as the acid concentrations (composition of solutions) were taken into account during the sorption process.

Effect of sodium chloride was considered due to the fact that palladium(II) and other noble metals in the form of alloys, sulphide minerals as well as native minerals can be converted to water-soluble sodium salts by heating the samples with sodium chloride in a stream of chloride at 853 K. Except the chlorination [3,11–14] the leaching process [3,14] using a mixture of mineral acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) was applied for the PGM metals. Due to this fact the chloride and chloride–nitrate solutions were examined, too. Moreover, many scrap metals are recovered pyro-metallurgically but most precious metals are frequently recovered by hydrometallurgical process or by combination of pyro- and hydro-metallurgical methods where solutions of similar compositions occurred [14]. Ion-exchange methods are mostly based on the separation of the anionic chloro complexes of the platinum group metals (PGMs) from the matrix elements which exist in cationic forms in dilute acid solutions. Anionic chloro complexes are selectively retained on the anion exchange resins, therefore the anion exchange resins such as Dowex MSA-1 and Dowex MSA-2 were applied in the sorption process of palladium(II) complexes.

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## Nomenclature

$C_0$	initial concentration of Pd(II) complexes (mg/dm <sup>3</sup> )
$C_r$	working ion exchange capacity (g/cm <sup>3</sup> )
$C_t$	concentration of Pd(II) after time $t$ (mg/dm <sup>3</sup> )
$D_v$	bed distribution coefficient
$D_m$	mass distribution coefficient
$d_z$	anion exchanger bed density
$m_j$	dry anion exchanger weight, $m_j = d_z \cdot V_j$ (g)
$q_t$	amount of Pd(II) complexes sorbed onto resin; sorption capacity (mg/g)
$t$	phases contact time (s)
$U$	effluent volume at $C = 0.5 C_0$ (cm <sup>3</sup> )
$U_0$	dead volume in the column (cm <sup>3</sup> )
$V$	volume of the solution (0.05 dm <sup>3</sup> )
$V_b$	speed of solution passed through the anion exchanger bed, 0.4 cm <sup>3</sup> /min
$V_j$	volume of anion exchanger bed put into the column (10 cm <sup>3</sup> )
$V_p$	collected volume of effluent between the first fraction and that to the breakthrough point (cm <sup>3</sup> )
$V_s$	stirring speed phases, 180 rpm
$V_v$	void (inter-particle) anion exchanger bed volume (which amount to ca. 0.4)
$W$	weight of the dry anion exchanger (0.5 g)

## 2. Experimental

### 2.1. Solutions preparation

Stock palladium(II) solution was prepared from solid palladium chloride (PdCl<sub>2</sub>; >99%, POCh, Poland). The mass required for a 0.056 M stock solution was weighed and boiled in hydrochloric acid until dissolution.

Aqueous chloride solutions (0.1–3.0 M HCl; 0.1–2.0 M HCl–1.0 M NaCl; 0.1–2.0 M HCl–2.0 M NaCl) of palladium(II) in the studies were prepared by dilution with concentrated HCl in order to obtain a desired value of H<sup>+</sup> concentration. The working solutions were found to contain 0.00056 M Pd(II). In the case of chloride solutions containing sodium chloride, a weighed amount of salt (POCh, Poland) was dissolved in distilled water before dilution with HCl.

The working chloride–nitrate solutions (0.1 M HCl–0.9 M HNO<sub>3</sub>; 0.2 M HCl–0.8 M HNO<sub>3</sub>; 0.5 M HCl–0.5 M HNO<sub>3</sub>; 0.8 M HCl–0.2 M HNO<sub>3</sub>; 0.9 M HCl–0.1 M HNO<sub>3</sub>) were obtained by dilution with HCl and HNO<sub>3</sub> to adjust the H<sup>+</sup> concentration to the desired value. All

other reagents, which were produced by POCh (Poland), were of analytical grade.

### 2.2. Anion exchange resins

The strongly basic anion exchange resins Dowex MSA-1 and Dowex MSA-2 were used in palladium(II) sorption from the chloride and chloride–nitrate solutions. The properties of applied anion exchange resins are presented in Table 1.

### 2.3. Methods

The sorption of palladium(II) complexes onto the strongly basic anion exchangers Dowex MSA-1 and Dowex MSA-2 was investigated using the batch method. Proper, dry anion exchange resin was weighed and then the amount (0.5 ± 0.0005 g) was shaken mechanically (thermostatic shaker; Elphin +358S, Poland) with 50 cm<sup>3</sup> of corresponding solutions (chloride or chloride–nitrate) for 1–720 min at 293 K. The stirring speed,  $V_s$ , of organic and aqueous phases was constant and equal to 180 rpm. At the end of the predominant time interval, the anion exchanger resin was removed by filtration and the palladium(II) complexes were determined using the spectrophotometric iodide method.

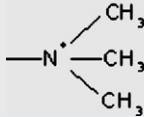
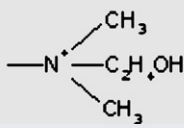
The breakthrough curves of palladium(II) complexes were determined using the dynamic method. The one-centimeter diameter columns were filled with the swollen strongly basic anion exchange resins Dowex MSA-1 and Dowex MSA-2 in the amount of 10 cm<sup>3</sup>. Then the palladium(II) chloride and chloride–nitrate solutions were passed through the anion exchanger beds at the rate,  $V_b$ , of 0.4 cm<sup>3</sup>/min and after the sorption process the eluate was collected in the fractions and the content of palladium(II) complexes was determined using the iodide method.

The FT-IR analysis was used to obtain spectra of palladium(II) before and after the sorption process. The 0.5 g samples of dry anion exchange resins were shaken mechanically with 50 cm<sup>3</sup> of 0.1 M HCl–1.0 M NaCl–100 mg/dm<sup>3</sup> Pd(II) solution for 240 min at 293 K. After stirring the loaded anion exchangers were separated from the solutions and dried at room temperature. Then the loaded anion exchangers were broken up and tableted with KBr and the FT-IR spectra were recorded. In order to compare spectra of palladium(II) before and after the sorption process, the spectra of unloaded anion exchangers were recorded, too.

### 2.4. Sorption parameters

Using the batch method the amount of palladium(II) complexes sorbed onto the anion exchangers,  $q_t$  (mg/g) was calculated by

**Table 1**  
Anion exchange resins characteristics.

Description	Dowex MSA 1	Dowex MSA 2
Structure	Macroporous	Macroporous
Type	Strongly basic, type 1 Trimethyloammonium	Strongly basic, type 2 Dimethyl-hydroxyethyl- quaternary amine
Functional groups		
Maximum operating temperature [K]	342	350
Matrix	Polystyrene–divinylbenzene	
Water retention [%]	56–64	48–56
Operating pH range	0–14	0–14
Total exchange capacity [eq/dm <sup>3</sup> ]	1.0	1.1

**Table 2**  
The sorption parameters obtained by means of the batch and dynamic methods.

Batch		Dynamic	
Amount of palladium (II) complexes sorbed onto anion exchangers	Working ion exchange capacity	Mass distribution coefficient	Bed distribution coefficient
$q_t$ (mg/g)	$C_r$ (g/cm <sup>3</sup> )	$D_m$	$D_v$
$q_t = (C_o - C_t)V/W$ (1)	$C_r = (V_p \times C_o)/V_j$ (2)	$D_m = (U - U_o - V_v)/m_j$ (3)	$D_v = D_m d_z$ (4)

means of the mass-balance relationship Eq. (1). Moreover, the working ion-exchange capacity,  $C_r$  (g/cm<sup>3</sup>) as well as the mass,  $D_m$  and bed,  $D_v$  distribution coefficients were calculated using Eqs. (2)–(4). The equations needed to calculate the above parameters are presented in Table 2.

### 2.5. Apparatus and analytical procedure

The spectrophotometer Specord M42; Carl Zeiss Jena, Germany was used to determine the concentration of palladium(II) by means of the UV-Vis, iodide method.

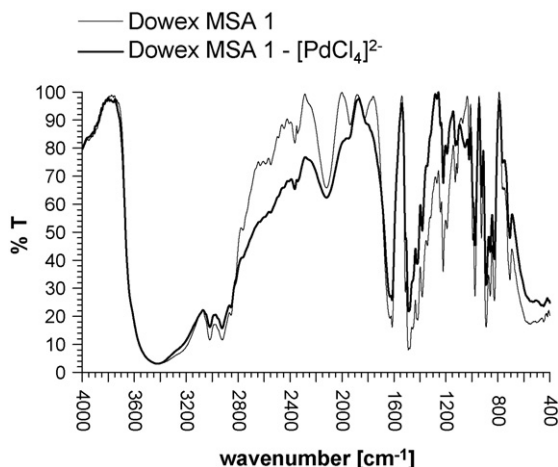
The FT-IR spectra were obtained using the spectrometer, type 175X, PerkinElmer, Germany.

The iodide method is based on the derivatization reaction with KI. Palladium(II) in the presence of an excess of KI formed the complex  $[PdI_4]^{2-}$  which are red-brown. The samples of unknown concentration of Pd(II) were prepared by addition of 5 cm<sup>3</sup> of 6 M HCl, then 10 cm<sup>3</sup> of 20% KI solutions and 2 cm<sup>3</sup> (chloride solutions) or 6 cm<sup>3</sup> (chloride-nitrate solutions) of 1% ascorbic acid depending on the solutions under determination. The solutions were diluted with distilled water and stirred. The absorbance of palladium(II) solutions was measured in the one-centimeter cell against blank test as the reference at the analytical wavelength,  $\lambda_{max} = 407$  nm [15,16].

## 3. Results and discussion

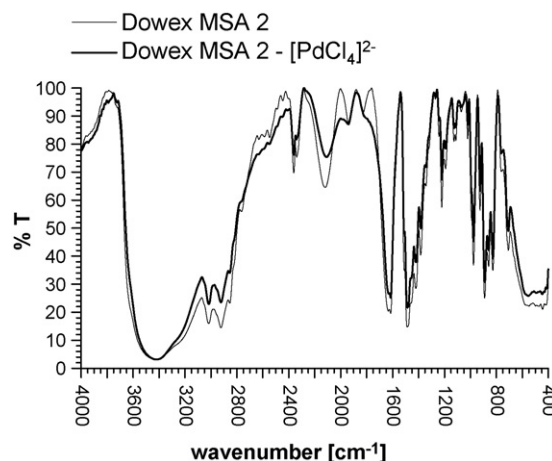
### 3.1. FT-IR analysis

The Fourier transform infrared spectroscopy (FT-IR) method was used in the studies of palladium(II) complexes sorption onto the strongly basic anion exchangers: Dowex MSA-1 and Dowex MSA-2. The spectra of the anion exchangers were measured within the range of 400–4000 cm<sup>-1</sup>. The spectra for the Dowex resins before and after loading with palladium(II) are shown in Figs. 1 and 2.

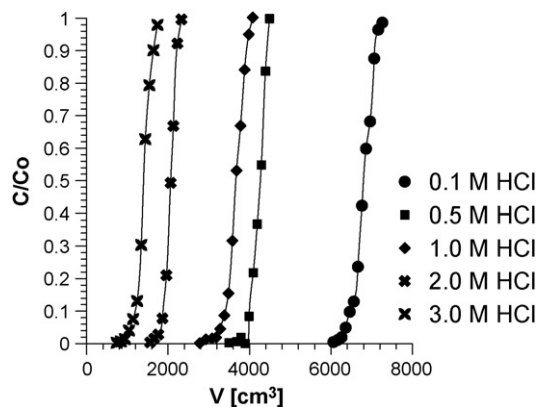


**Fig. 1.** FT-IR spectra for Dowex MSA-1 before and after sorption of Pd(II) ( $T = 293$  K,  $t = 240$  min,  $V_s = 180$   $\Gamma$ pm,  $V = 0.05$  dm<sup>3</sup>,  $W = 0.5$  g).

In the higher frequency region (the peak around 3442 cm<sup>-1</sup>), a very strong and broad band of the O–H stretching vibrations was observed for both anion exchangers. On the lower frequency side of this band some peaks at about 3018, 2922, 2858 cm<sup>-1</sup> appeared. The above mentioned peaks related to the symmetric or asymmetric, stretching vibrations of the ring C–H bonds and –CH<sub>2</sub> groups of the matrix (cross-linked polystyrene) of the anion exchangers (3018 cm<sup>-1</sup>  $\nu_{as}(C-H)$ ; 2922 cm<sup>-1</sup>  $\nu_{as}(-CH_2)$ ; 2858 cm<sup>-1</sup>  $\nu_s(-CH_2)$ ). Moreover, the vibrations of the O–H group come from the water, present in the anion exchanger phase appeared at 1615 cm<sup>-1</sup> ( $\delta(O-H)$  for all anion exchangers. The asymmetric, stretching vibrations of carbon–carbon bonds in the ring ( $\nu_{as}(C=C)$ ) as well as the asymmetric, scissoring vibrations of methylene groups ( $\delta_{as}(-CH_2)$ ) appeared at 1487, 1421, 1383 cm<sup>-1</sup>. The deformation vibrations of 1,4-disubstituted benzene ring coming from the styrene–divinylbenzene matrix of resins (S–DVB) were also observed at 976 and 826 cm<sup>-1</sup> [17–19].



**Fig. 2.** FT-IR spectra for Dowex MSA-2 before and after sorption of Pd(II) ( $T = 293$  K,  $t = 240$  min,  $V_s = 180$   $\Gamma$ pm,  $V = 0.05$  dm<sup>3</sup>,  $W = 0.5$  g).



**Fig. 3.** Breakthrough curves of Pd(II) for Dowex MSA-1 for the 0.1–3.0 M HCl solutions ( $C_o = 0.00056$  M,  $V_b = 0.4$  cm<sup>3</sup>/min,  $V_j = 10$  cm<sup>3</sup>).

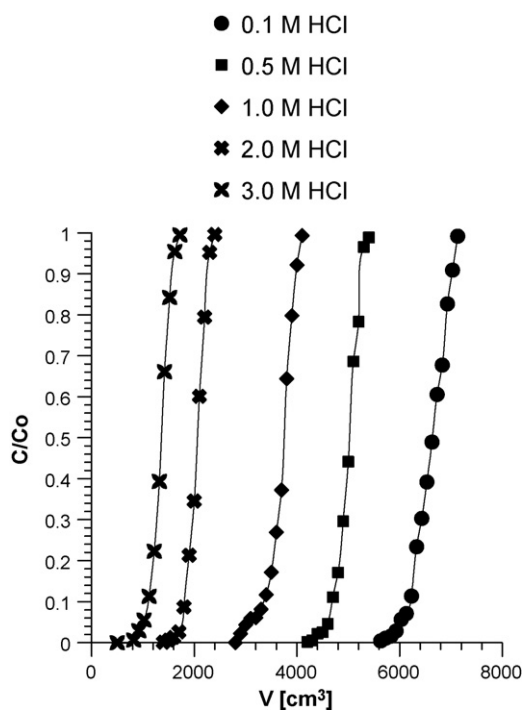


Fig. 4. Breakthrough curves of Pd(II) for Dowex MSA-2 for the 0.1–3.0 M HCl solutions ( $C_0 = 0.00056$  M,  $V_b = 0.4$  cm<sup>3</sup>/min,  $V_j = 10$  cm<sup>3</sup>).

As follows from the recorded spectra (Figs. 1 and 2) of the strongly basic anion exchangers before and after the sorption process of palladium(II), the peaks and their positions on spectra are very similar in the range of wave number from 975 to 400 cm<sup>-1</sup> and 1614 to 400 cm<sup>-1</sup> for Dowex MSA-1 and Dowex MSA-2, respectively but the intensity of some bands changed after the sorption process. In the higher frequency region from 2500 to 1600 cm<sup>-1</sup> differences between unloaded resin's spectra and those after loading appeared

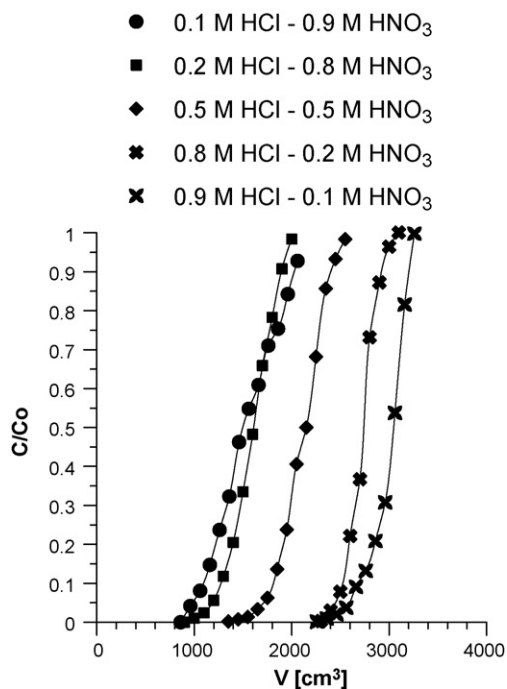


Fig. 5. Breakthrough curves of Pd(II) for Dowex MSA-1 for the 0.1–0.9 M HCl–0.9–0.1 M HNO<sub>3</sub> solutions ( $C_0 = 0.00056$  M,  $V_b = 0.4$  cm<sup>3</sup>/min,  $V_j = 10$  cm<sup>3</sup>).

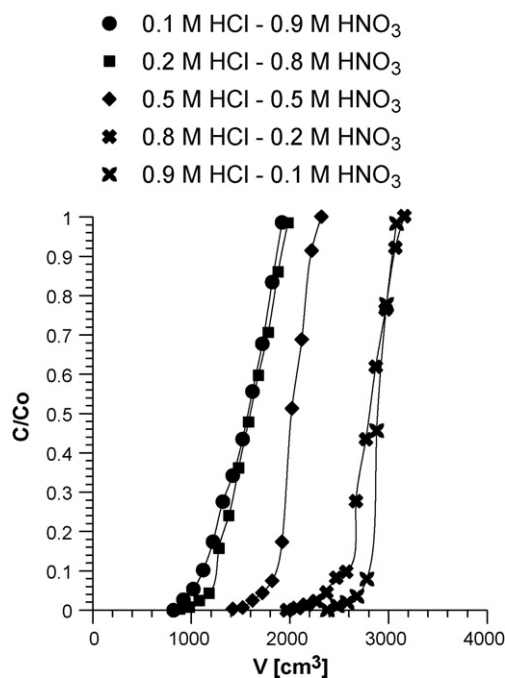


Fig. 6. Breakthrough curves of Pd(II) for Dowex MSA-2 for the 0.1–0.9 M HCl–0.9–0.1 M HNO<sub>3</sub> solutions ( $C_0 = 0.00056$  M,  $V_b = 0.4$  cm<sup>3</sup>/min,  $V_j = 10$  cm<sup>3</sup>).

for both resins. Before the sorption process, the peaks at 1827 and 1938 cm<sup>-1</sup> are found for both resins whereas after sorption these peaks disappeared.

### 3.2. Column experiments

The breakthrough curves of palladium(II) were obtained by means of dynamic method and presented in Figs. 3–6 for the strongly basic anion exchange resins Dowex MSA-1 and Dowex MSA-2, respectively. Using these curves the sorption parameters such as the working ion exchange capacities,  $C_r$  as well as the mass,  $D_w$  and bed,  $D_m$  distribution coefficients were calculated and given in Table 3. The results (Figs. 3–6 and Table 3) indicate that the sorption parameters for the chloride (HCl) and chloride–nitrate (HCl–HNO<sub>3</sub>) solutions depend on acid(s) concentration. In the chloride solutions (HCl)  $C_r$ ,  $D_w$ ,  $D_m$  values decrease with the increasing hydrochloric acid concentration for the anion exchangers under discussion. The reverse trend is observed in the chloride–nitrate solutions where the sorption parameters increase with the increasing hydrochloric acid concentration or with the increasing ratio of hydrochloric acid to nitric acid. When the HCl:HNO<sub>3</sub> ratio is 1:9, the sorption parameters achieve the smallest values. The changes in  $C_r$ ,  $D_w$  and  $D_m$  values in the chloride and chloride–nitrate solutions could have been caused by competitive sorption of Cl<sup>-</sup> and HCl<sub>2</sub><sup>-</sup> and the increasing competition between Cl<sup>-</sup> and metal-complex anions as well as competitive sorption between NO<sub>3</sub><sup>-</sup> and H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup> ions, respectively [20–22].

The highest differences in the working anion exchange capacities for Dowex MSA-1 and Dowex MSA-2 are observed in the 0.1 and 0.5 M HCl solutions whereas in the 1.0–3.0 M HCl and the chloride–nitrate solutions  $C_r$  values are really similar for both resins. Strong bases are protonated much more readily than weak bases and this indicates that they can behave as ion exchangers at relatively low acid concentrations.

The similar results obtained for Dowex MSA-1 and Dowex MSA-2 are due to the fact that both resins belong to the same type: the strongly basic anion exchange resin. Dowex MSA-2 as the strongly basic anion exchange resin, type 2 possesses the dimethyl-

**Table 3**  
The calculated values of sorption parameters for the chloride (HCl) and chloride–nitrate (HCl–HNO<sub>3</sub>) solutions.

Systems	Dowex MSA-1 <sup>a</sup>			Dowex MSA-2 <sup>b</sup>		
	$C_r$ (g/cm <sup>3</sup> )	$D_w$	$D_m$	$C_r$ (g/cm <sup>3</sup> )	$D_w$	$D_m$
0.1 M HCl	0.0616	2478.8	679.2	0.0563	2388.0	663.4
0.5 M HCl	0.0369	1553.3	425.6	0.0430	1806.7	501.9
1.0 M HCl	0.0293	1334.3	365.6	0.0280	1347.7	374.4
2.0 M HCl	0.0156	749.6	205.4	0.0150	740.1	205.6
3.0 M HCl	0.0084	508.0	139.2	0.0082	487.4	135.4
0.1 M HCl–0.9 M HNO <sub>3</sub>	0.0086	544.5	149.2	0.0082	564.4	156.8
0.2 M HCl–0.8 M HNO <sub>3</sub>	0.0090	585.4	160.4	0.0088	572.7	159.1
0.5 M HCl–0.5 M HNO <sub>3</sub>	0.0135	782.5	214.4	0.0132	722.8	200.8
0.8 M HCl–0.2 M HNO <sub>3</sub>	0.0220	998.2	273.5	0.0197	1007.9	280.0
0.9 M HCl–0.1 M HNO <sub>3</sub>	0.0226	1110.2	304.2	0.0238	1037.8	288.3

<sup>a</sup>  $d_2 = 0.2740$  g/cm<sup>3</sup>.

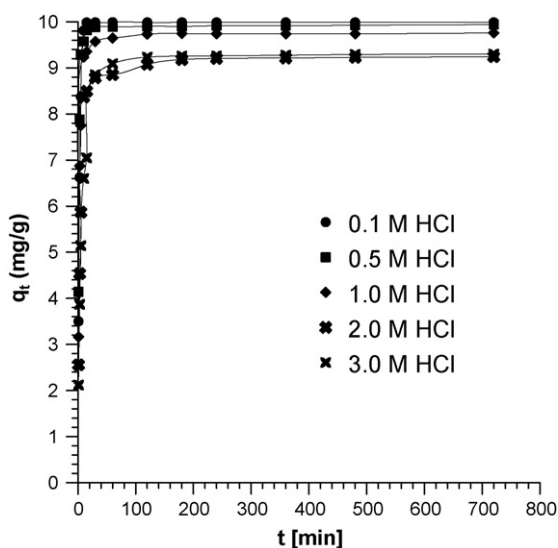
<sup>b</sup>  $d_2 = 0.2778$  g/cm<sup>3</sup>.

hydroxyethyl-quaternary amine group ( $-N^+(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ ) which supplies more coordination atoms. The functional groups of Dowex MSA-1 contain only one type of donor atom, nitrogen atom whereas the functional groups of Dowex MSA-2 contain N and O donor atoms. This fact should influence on the working ion exchange capacity resulting in their values growth, but in this case it does not hold. During the sorption of palladium(II) complexes, the same mechanism of sorption onto Dowex MSA-1 and Dowex MSA-2 takes place. The anion-exchange as well as the chelating mechanism is occurring. Moreover, the total ion exchange capacity which is given by the producer of anion exchangers (Dow Chemical Co., USA) is of similar values. The above facts point to similar results during the sorption process of Pd(II) complexes.

According to hard and soft acids and bases theory (HSAB), the anion exchangers of the functional groups containing one or more donor atoms interact strongly with soft acids like PGM metals. This fact and the presented results indicate that both strongly basic anion exchange resins can be applied in palladium(II) complexes sorption with high efficiency [22].

### 3.3. Effect of phases contact time

A series of contact time experiments for palladium(II) complexes sorption was carried out. Figs. 7 and 8 display the influence of phases contact time onto sorption capacity,  $q_t$  (mg/g) of Pd(II) com-

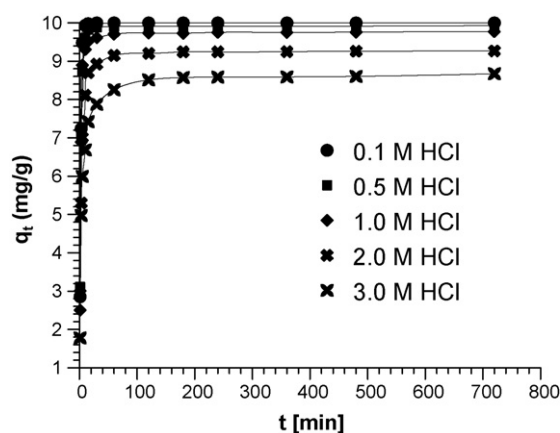


**Fig. 7.** Effect of phases contact time on sorption capacity,  $q_t$  (mg/g) for Dowex MSA-1 from the chloride solutions ( $T = 293$  K,  $V_s = 180$   $\Gamma$ pm,  $W = 0.5$  g,  $V = 0.05$  dm<sup>3</sup>).

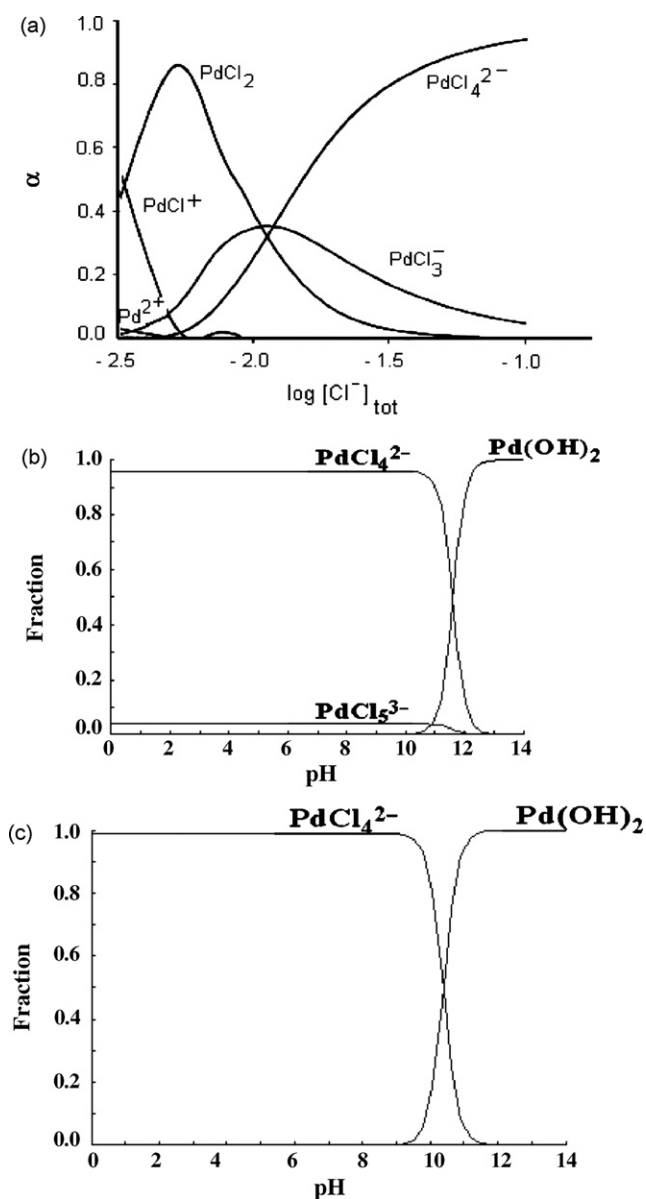
plexes from the chloride solutions for Dowex MSA-1 and Dowex MSA-2, respectively. The amount of palladium(II) complexes sorbed onto the anion exchange resins,  $q_t$  (Figs. 7 and 8) increase with time. At the beginning when the phases contact time is small, changes of sorption capacities values are the highest and then decrease until the equilibrium is reached. After 15 min the equilibrium is reached in the 0.1 M HCl solutions for both resins under discussion and the curves are a straight line, the plateau is observed. Also in the case of other chloride solutions plateau occurs after a longer period of time; 30, 120 and 180 min for the 0.5; 1.0 and 2.0–3.0 M HCl solutions, respectively. Similar changes of sorption capacities with time  $t$  are observed in the chloride–nitrate solutions (not presented). The amounts of Pd(II) sorbed onto the Dowex resins are 8.6; 8.7; 9.3; 9.6; 9.7 for the phases contact time equal 720 min and for the 0.1 M HCl–0.9 M HNO<sub>3</sub>, . . . 0.9 M HCl–0.1 M HNO<sub>3</sub> solutions, respectively. The phase equilibrium in the case of the chloride–nitrate solutions appears after 60–120 min.

### 3.4. Distribution of palladium(II) complexes in aqueous solution

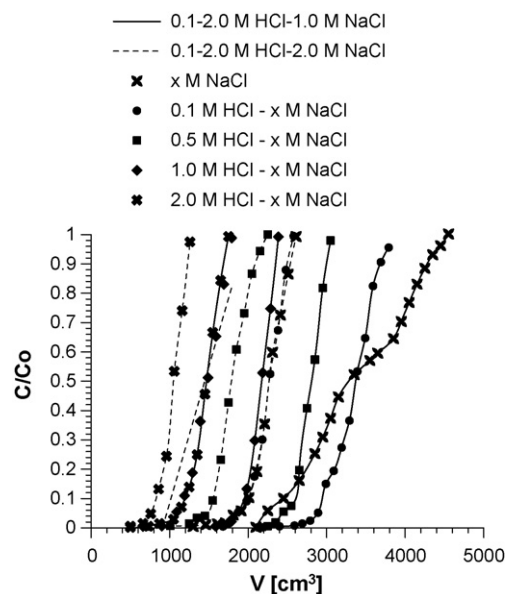
Palladium(II) in chloride solutions can form different stable complexes such as: chloride ( $\text{PdCl}^+$ ,  $\text{PdCl}_2$ ,  $\text{PdCl}_3^-$ ,  $\text{PdCl}_4^{2-}$ ), hydroxy-chloride ( $\text{PdCl}_3(\text{OH})^{2-}$ ,  $\text{PdCl}_2(\text{OH})_2^{2-}$ ,  $\text{PdCl}(\text{OH})_3^{2-}$ ) as well as hydroxide ( $\text{Pd}(\text{OH})_2$ ,  $\text{Pd}(\text{OH})_4^{2-}$ ). The anion exchange reaction is possible due to the fact that anion complexes are capable of undergoing ion exchange reactions onto anionic exchangers. Besides, the anionic species of Pd(II) complexes are more favourable than other for anion exchange resins.



**Fig. 8.** Effect of phases contact time on sorption capacity,  $q_t$  (mg/g) for Dowex MSA-2 from the chloride solutions ( $T = 293$  K,  $V_s = 180$   $\Gamma$ pm,  $W = 0.5$  g,  $V = 0.05$  dm<sup>3</sup>).



**Fig. 9.** Distribution diagram of metal species vs. (a)  $\log [Cl^-]_{tot}$  ( $[Pd^{2+}]_{tot} = 10.0 \mu M$ ); (b) pH ( $[Pd^{2+}]_{tot} = 0.00056$ ,  $[Cl^-]_{tot} = 1 M$ ); (c) ( $[Pd^{2+}]_{tot} = 0.00056$ ,  $[Cl^-]_{tot} = 4 M$ ).



**Fig. 10.** Effect of sodium chloride concentration on the breakthrough curves of Pd(II) for Dowex MSA-1 ( $C_0 = 0.00056 M$ ,  $V_b = 0.4 cm^3/min$ ,  $V_j = 10 cm^3$ ).

The distribution diagram of palladium species vs.  $\log [Cl^-]_{tot}$  and pH for 1.0 M NaCl and 2.0 M HCl–2.0 M NaCl are presented in Fig. 9(a–c). The variation of HCl concentration has a double effect on Pd(II) sorption. While the pH of the metal ions solution basically does not influence the sorption of Pd(II) the different of  $Cl^-$  concentration leads to a different distribution of chloro complexes of Pd(II). When  $[Cl^-]$  is equal to 0.01 the complexes  $PdCl_4^{2-}$ ,  $PdCl(H_2O)_3^-$ ,  $PdCl_2(H_2O)_2$  are formed. In solutions containing  $[Cl^-] = 0.1 M$  the predominant species of Pd(II) is  $PdCl_4^{2-}$  (95%) whereas for concentration of  $[Cl^-]$  less than 0.001 M cationic species such as  $PdCl(H_2O)_3^+$ ,  $PdCl^+$ ,  $Pd(OH)^+$  are formed [22,23].

### 3.5. Effect of acid(s) concentration

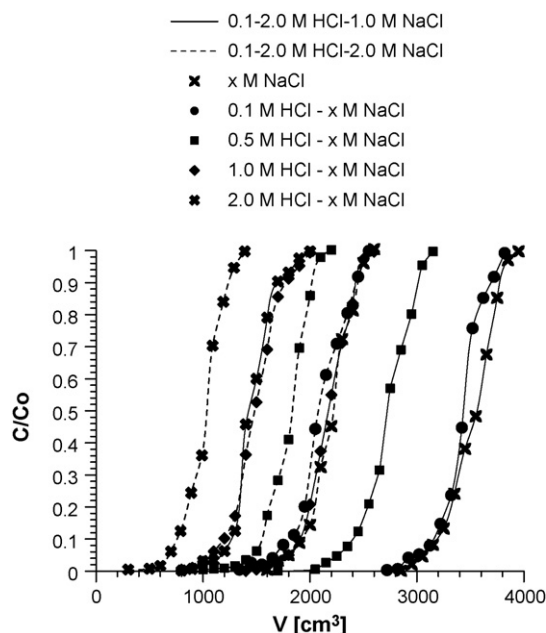
Acids concentration as well as ionic strength of solutions influence the sorption capacity,  $q_t$ . The effect of hydrochloric acid concentration on  $q_t$  values in the chloride solutions is higher for Dowex MSA-2. In the case of Dowex MSA-1,  $q_t$  values negligibly decrease with the increasing hydrochloric acid concentration. The smallest values of the sorption capacity are in the 3.0 M HCl solution. In the case of the chloride–nitrate solutions,  $q_t$  values are similar to those for Dowex MSA-1 and Dowex MSA-2. Moreover, the effect of hydrochloric and nitric acid concentrations on  $q_t$  values is really insignificant. The smallest  $q_t$  values are observed in the

**Table 4**  
Effect of sodium chloride concentration onto the sorption parameters.

Systems	Dowex MSA-1 <sup>a</sup>			Dowex MSA-2 <sup>b</sup>		
	$C_r$ (g/cm <sup>3</sup> )	$D_w$	$D_m$	$C_r$ (g/cm <sup>3</sup> )	$D_w$	$D_m$
1.0 M NaCl	0.0210	1194.2	327.2	0.0285	1280.1	355.6
0.1 M HCl–1.0 M NaCl	0.0240	1225.9	335.9	0.0282	1234.3	342.9
0.5 M HCl–1.0 M NaCl	0.0225	1021.5	279.9	0.0215	977.0	271.4
1.0 M HCl–1.0 M NaCl	0.0169	790.5	216.6	0.0150	779.7	216.6
2.0 M HCl–1.0 M NaCl	0.0087	534.3	146.4	0.0090	510.8	141.9
2.0 M NaCl	0.0146	824.5	225.9	0.0160	797.7	221.6
0.1 M HCl–2.0 M NaCl	0.0168	825.2	226.1	0.0134	745.5	207.1
0.5 M HCl–2.0 M NaCl	0.0101	649.6	178.0	0.0120	658.7	183.0
1.0 M HCl–2.0 M NaCl	0.0090	538.3	147.5	0.0090	531.3	147.6
2.0 M HCl–2.0 M NaCl	0.0066	380.3	104.2	0.0050	370.8	103.0

<sup>a</sup>  $d_s = 0.2740 g/cm^3$ .

<sup>b</sup>  $d_s = 0.2778 g/cm^3$ .

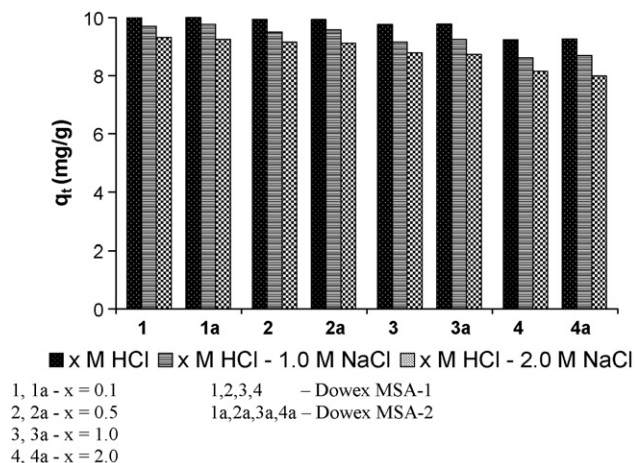


**Fig. 11.** Effect of sodium chloride concentration on the breakthrough curves of Pd(II) for Dowex MSA-2 ( $C_0 = 0.00056$  M,  $V_0 = 0.4$  cm<sup>3</sup>/min,  $V_j = 10$  cm<sup>3</sup>).

solutions where the HCl:HNO<sub>3</sub> ratio is 1:9. The sorption capacities achieve very high values in all solutions under discussion.

### 3.6. Effect of sodium chloride addition

Effect of sodium chloride addition as well as its concentration which changes in the range 1.0–2.0 M on the palladium(II) complexes sorption was examined. As follows from the presented results obtained by means of column studies (Table 4 and Figs. 10–12) sodium chloride addition causes considerable drop of the working anion exchange capacities as well as the mass and bed distribution coefficients. Moreover, concentration of sodium chloride also affects the sorption yield.  $C_r$ ,  $D_w$ ,  $D_m$  values decrease with the increasing sodium chloride concentration. The smallest values of the working anion exchange capacities, 0.0066 and 0.0050 g/cm<sup>3</sup> for Dowex MSA-1 and Dowex MSA-2, respectively are observed in the 2.0 M HCl–2.0 M NaCl solutions.



**Fig. 12.** Sorption capacities in the chloride solutions with the addition of sodium chloride for Dowex MSA-1 and Dowex MSA-2 ( $t = 720$  min,  $T = 293$  K,  $V_s = 180$  Γpm).

The sorption capacities determined by means of static method depend on sodium chloride addition, too. Fig. 11 presents the amount of palladium(II) complexes sorbed on Dowex MSA-1 and Dowex MSA-2 in the solution containing 1.0 and 2.0 M NaCl (phases contact time,  $t = 720$  min). In this case the sorption capacities achieve smaller values than in the chloride solutions without this salt.

Sodium chloride addition causes increase of ionic strength of solutions which leads to decrease of  $q_t$ ,  $C_r$ ,  $D_w$ ,  $D_m$  values.

## 4. Conclusion

The presented results lead to the following conclusions:

- The strongly basic anion exchange resins type 1–Dowex MSA-1 and type 2–Dowex MSA-2 are very efficient in the palladium(II) complexes sorption from the chloride and chloride–nitrate solutions.
- The working anion exchange capacity as well as the mass and bed distribution coefficients depends on hydrochloric acid concentration. Sorption parameters decrease and increase with the increasing HCl concentration for the chloride and chloride–nitrate solutions, respectively.
- Taking into account the values of working ion exchange capacities,  $C_r$  the following series of the Dowex resins towards Pd(II) complexes are shown:

- 0.1 M HCl  
Dowex MSA-1 (0.0616 g/cm<sup>3</sup>) > Dowex MSA-2 (0.0563 g/cm<sup>3</sup>)
- 0.5 M HCl  
Dowex MSA-2 (0.0430 g/cm<sup>3</sup>) > Dowex MSA-1 (0.0369 g/cm<sup>3</sup>)
- 1.0 ÷ 3.0 M HCl;
- 0.1–0.9 M HCl–0.9–0.1 M HNO<sub>3</sub>  
Dowex MSA-1 ≈ Dowex MSA-2

- The sodium chloride addition as well as the concentration of salt affects negatively the palladium(II) complexes sorption yield onto the Dowex resins causing their drop with the increasing NaCl concentration.
- The mechanism of palladium(II) complexes binding is the anion-exchange and/or chelating.
- The amount of palladium(II) complexes sorbed onto the Dowex resins increases with the increasing phases contact time.
- The best operating conditions of the sorption process of Pd(II) onto the Dowex resins from solutions under discussion are: concentration of solution, 0.1 M, phases contact time,  $t = 30$  min (chloride solutions) and the ratio HCl:HNO<sub>3</sub> 9:1,  $t = 60$  min (chloride–nitrate solutions), anion exchangers dose = 0.5 g and  $T = 293$  K.

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