SELECTIVITY COEFFICIENTS OF SOME SIMPLE AND COMPLEX INORGANIC IONS FOR SPHERON DEAE

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The selectivity coefficients of the nitrate and chloride ions and of anionic chloro complexes of Au(III), Rh(III), Pd(II), and Pt(IV) for ion exchange on Spheron DEAE in the chloride form are determined by the dynamic method. The complex anion species formed are identified and the ion exchange nature of the sorption of precious metals on this sorbent is confirmed based on the elution order of the precious metals as determined previously by the column chromatgraphy on Spheron DEAE using hydrochloric acid as the mobile phase. The effect of the presence of perchlorate in the mobile phase during the liquid chromatography of precious metals and during the chromatographic determination of nitrate traces is explained.

Spheron DEAE has been applied with advantage to the chromatographic separation and determination of platinum, palladium and rhodium[1], sorption of gold[2,3], as well as the determination of nitrate in some foods[4]. When seeking for a suitable composition of the mobile phase, perchlorate was often observed to have a favourable effect on the capacity ratios of the components determined, of which use has been made in the analytical procedures developed. We have suggested[1] that the elution order of platinum metals, and thus also their capacity ratios, are related to the selectivity coefficients of the corresponding anions assuming the retention of these ions by the ion exchange mechanism rather than complex formation as supposed for the sorption of platinum metals on other sorbents with similarly weakly basic functional groups[5].

The selectivity coefficients for Spheron DEAE have not been so far published. In order to contribute to the elucidation of the sorption mechanism of complex anions of precious metals, and also to make it possible for the effect of perchlorate on the capacity ratios to be explained, we determined the selectivity coefficients of the precious metal anions as well as of the simple nitrate and perchlorate ions.

EXPERIMENTAL

Chemicals and Solutions

Common chemicals were of reagent grade (Lachema, Brno), solutions were made up using

deionized water. Solutions of gold, platinum and palladium chloro complexes (10—5 mmol l^{-1}) were obtained by dissolving the pure metals (Safina, Vestec) in *aqua regia*. Rhodium was dissolved in hydrochloric acid under pressure[6] with an addition of oxidant ($c_{Rh} \approx 10$ mmol l^{-1}). The solutions of the precious metals were evaporated to dryness with a 10% amount of substance excess of sodium chloride and the nitroso complexes were decomposed by double evaporation of the solutions with hydrochloric acid to dryness. The residues were dissolved in water after addition of hydrochloric acid such that its concentration in the stock solution was 0·1 mol l^{-1}. The stock solutions of sodium perchlorate and sodium nitrate were obtained from chemicals dried at 105 and 150°C, respectively.

Sorbent

The sorbent was Spheron DEAE 1000 (Lachema, Brno), $d_p = 0{\cdot}063-0{\cdot}100$ mm. Finer particles were removed by decantation after swirling and a 3 min standing. The sorbent was doubly recycled with NaOH, NaCl and HCl solutions in a concentration of 2 mol l^{-1}; between these, the sorbent was always washed with water and dried in air. The theoretical exchange capacity, calculated based on the determined nitrogen content, was $Q(N) = 1{\cdot}46$ mmol g^{-1} dry substance (dried in vacuum over P_2O_5 at room temperature) or 1·34 mmol g^{-1} (dried at 105°C) or 1·48 mmol g^{-1} (dried in air at room temperature and recalculated for the drying in vacuum). The practical exchange capacity was determined by titration of the eluted chloride[7]; this value was $Q(Cl) = 1{\cdot}47$ mmol g^{-1} dry substance (dried in vacuum).

Apparatus

The photometric measurements were performed on a VSU 2-P spectrophotometer (Carl Zeiss' Jena), the potentiometric titrations were carried out on an E 436 potentiograph equipped with a combined silver electrode (all Metrohm, Herisau). An OP 201/2 pH-meter fitted with an OP 0807P combined glass electrode (all Radelkis, Budapest), calibrated with NBS standard buffers, was used for the pH measurements. Homemade small glass columns featuring a negligible extra-column volume (column i.d. 6 mm, $V_c \approx 1$ ml, extra-column volume 10 µl) were used in conjuction with an SF 62 fraction collector (Laboratorní přístroje, Prague).

Analytical Methods

The platinum metals and gold were determined by measuring the absorbance of their chloro complexes in the UV region[8-10] (Au 314 nm, Pt 262 nm, Pd 224 nm, Rh 225 nm). Perchlorate was determined *via* absorbance of tris(2,2′-bipyridyl)iron(II) perchlorate after extraction into nitrobenzene[11], nitrate was determined *via* nitration of chromotropic acid[12]. The regression coefficients for the dependence $A = f(c)$ were calculated and the fit to the experimental points was evaluated in terms of the correlation coefficients ($r = 0{\cdot}9970-0{\cdot}9999$).

Sorption and Desorption Breakthrough Curves

The columns were packed with 200 mg of air-dried sorbent (*i.e.*, 167·4 mg of dry matter) ($V_c \approx$ $\approx$ 1 ml) and washed with sodium chloride or hydrochloric acid solution (0·1 mol l^{-1}) according to the influent solution used (NaCl or HCl). The concentration of the sorbed ion in the influent was 0·5—5 mmol l^{-1}. Fractions were collected in 5 min intervals and their volumes were determined by weighing. After the concentration of the ion in effluent became equal to that in influent, the column was washed with a $3V_c$ volume of water, followed by desorption.

The conditions for the sorption and desorption of the anions treated are given in Table I. The concentration of the ions in effluent was determined photometrically. Prior to the determination of gold, its complex with thiourea and the excess of the latter had to be decomposed[3].

Determination of Selectivity Coefficients

The sorptions and desorptions were conducted at a flow rate of 0·5 ml min^{-1} under conditions identical with those used for the study of the breakthrough curves. The effuent volumes in the sorption and desorption were determined based on these curves (Table I). The concentrations of the ions in eluate were determined photometrically. Each selectivity coefficient was obtained as the average of triplicate measurements under given conditions, and its confidence interval was calculated by means of Lord's distribution for the 95% probability level.

RESULTS AND DISCUSSION

The selectivity coefficients were determined by the direct dynamic method[13] which furnishes data describing the chromatographic separation phenomena better than the static methods. Indirect methods based on chromatographic data measurements were avoided for the selectivity coefficients to be obtained by a method other than chromatography.

For an exchange reaction

$$\overline{z\,Cl^-} + A^{z-} \rightleftharpoons \overline{A^{z-}} + z\,Cl^-\,, \qquad (A)$$

where the barred symbols refer to the species bonded in the sorbent, the selectivity coefficient is defined as

$$K^{A}_{zCl} = \eta_A[Cl^-]^z/\eta^z_{Cl}[A^{z-}]\,, \qquad (1)$$

where η's are the amount-of-substance contents (in mol g^{-1}) of the ions in the sorbent and the bracketed symbols are their equilibrium concentrations (in mol l^{-1}) in the outer solution. The η_A value was calculated as

$$\eta_A = c_{A,el}V_{el}/m_d\,, \qquad (2)$$

where $c_{A,el}$ is the concentration of A in the eluate volume V_{el} after the desorption and m_d is the dry weight of the sorbent, and η_{Cl} was calculated from the practical exchange capacity $Q(Cl)$ as

$$\eta_{Cl} = Q(Cl) - z\eta_A\,. \qquad (3)$$

The calculation of K^{A}_{zCl} thus requires that the charge of the ion sorbed, z, be known, which for complex anions of precious metals is quite a problem because of the possible simultaneous occurrence of several complex species in the solution. The sorption

was conducted at a constant ionic strength of $I = 0{\cdot}1$ and a constant total concentration of chloride in influent of $0{\cdot}1\ \mathrm{mol\,l^{-1}}$, and the pH was never higher than 1·3. The diagram of the predominating occurrence regions in the Au(III)–OH^-–Cl^- system[14] indicates that in such circumstances, nearly all gold is present as $[AuCl_4]^-$. According to the stepwise stability constants of platinum chloro complexes ($K_5 = 10^{3.70}$, $K_6 = 10^{2.22}$ at $I = 0{\cdot}5$, ref.[15]), a solution with $c_{Cl^-} = 0{\cdot}1\ \mathrm{mol\,l^{-1}}$ will contain about 6% $[Pt(H_2O)Cl_5]^-$, the remainder will be $[PtCl_6]^{2-}$. This ratio will vary in favour of the monovalent ion as this species is sorbed. The charge of the sorbed ion would not change on hydrolysis such as giving rise to the $[Pt(OH)Cl_5]^{2-}$ species. In the conditions applied, palladium should not yet form hydroxo complexes[16] $[Pd(OH)_xCl_y]^{2-x-y}$ and it should be present predominantly as $[PdCl_4]^{2-}$ or $[Pd(H_2O)Cl_3]^-$ (ref.[17]). According to the stability constants of rhodium chloro complexes[18], the $[Rh(H_2O)Cl_5]^{2-}$ and $[Rh(H_2O)_2Cl_4]^-$ species should exist in solution under the conditions used; their hydrolysis need not be taken into account at pH < 2·9 (ref.[19]).

Based on the experimental η_A, η_{Cl}, and $[A^{z-}]$ values and the known equilibrium concentration of chloride, the K^A_{zCl} values were calculated for the sorption of ClO_4^-, NO_3^-, and $AuCl_4^-$ ions, the charges of which are unambiguous. For the remaining ions, two possibilities were always considered, *viz.* the sorption of $[PtCl_6]^{2-}$ or

TABLE I

Conditions for the sorption and desorption of the ions studied; concentrations in the influent (c) and total volume of the effluent (V)

Anion	sorption				desorption		
	c_A mmol l^{-1}	c_{NaCl} mol l^{-1}	c_{HCl} mol l^{-1}	V ml	c_{NaCl} mol l^{-1}	c_{HCl} mol l^{-1}	V ml
ClO_4^-	0·495	0·10	—	150	0·10	—	250
ClO_4^-	5·01	—	0·10	50	—	1·0	50
NO_3^-	0·501	0·10	—	100	0·10	—	100
NO_3^-	5·01	—	0·10	60	—	1·0	25
$AuCl_x^{3-x}$	5·10	—	0·10	100	—	0·25[a]	50
$PtCl_x^{4-x}$	5·10	—	0·10	50	—	0·1[b]	10
$PdCl_x^{2-x}$	5·10	—	0·10	50	—	1·0	250
$RhCl_x^{3-x}$	0·577	0·05	0·05	10	0·10	—	10
$RhCl_x^{3-x}$	4·23	—	0·10	10	—	1·0	10

[a] With an addition of 0·4 mol l^{-1} of thiourea, [b] with an addition of 2·0 mol l^{-1} of $HClO_4$.

$[Pt(H_2O)Cl_5]^-$, $[PdCl_4]^-$ or $[Pd(H_2O)Cl_3]^-$, and $[Rh(H_2O)Cl_5]^{2-}$ or $[Rh(H_2O).$ $.Cl_4]^-$. The charge of the sorbed ion was inferred from the elution order of the ions as found previously[1], hence, from their capacity ratios k. Since the order of the latter for the eluted species is the same as the order of their mass distribution ratios D_m and, for a given column, also as the order of their distribution coefficients D_g ($D_g(A) = \eta_A/c_A$, where η_A is the amount-of-substance content of A in the sorbent and c_A is the total concentration of A in the outer solution), the order of the capacity ratios should be the same as the order of the selectivity coefficients.

In view of this, the sorption of the $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$ species is ruled out inasmuch as the calculated values of $K_{2Cl}^{PdCl_4} = 2\,450$ and $K_{2Cl}^{PtCl_6} = 22\,900$ would be higher than $K_{Cl}^{AuCl_4} = 160$ in contrast to the observed chromatographic behaviour of the chloro complexes of these precious metals ($k_{Au} > k_{Pt} > k_{Pd}$). As to rhodium, the species carrying a unit charge is again preferred, this being consistent with the very low capacity ratio of rhodium found for still higher chloride concentrations[1] ($1-5$ mol l^{-1}). The charge of -1 was also confirmed[1] by the $\log k = f(a_{Cl^-})$ dependence. The selectivity coefficient values, along with the experimental conditions used, are given in Table II.

The selectivity coefficients found thus agree with the previously established effect of perchlorate in the mobile phase on the retention times of nitrate and platinum metals chloro complexes. The selectivity coefficients for perchlorates, nitrates, and tetrachloroaurates(III) are unambiguous, the remaining coefficients are valid provided that the anions sorbed are monovalent; this assumption has been verified previously

TABLE II

Selectivity coefficients of some anions on Spheron DEAE

Anion A^{z-}	$c_{A,init}$ mmol l^{-1}	c_{NaCl} mol l^{-1}	c_{HCl} mol l^{-1}	K_{zCl}^{A} [a]
ClO_3^-	0·50	0·1	—	43·4 ± 0·8
	5·0	—	0·1	26·0 ± 0·8
NO_3^-	0·50	0·1	—	2·79 ± 0·07
	5·0	—	0·1	3·2 ± 0·7
$[AuCl_4]^-$	5·1	—	0·1	160 ± 12
$[Pt(H_2O)Cl_5]^-$	5·1	—	0·1	53 ± 4
$[Pd(H_2O)Cl_3]^-$	5·1	—	0·1	19 ± 6
$[Rh(H_2O)_2Cl_4]^-$	0·60	0·05	0·05	0·035 ± 0·004
	4·2	—	0·1	0·295 ± 0·005

[a] Confidence interval calculated from three measurements for the 95% probability is given.

for Pd and Rh using an independent approach[1]. The selectivity coefficients of the precious metal anions give an additional evidence of the ions exchange nature of their sorption on Spheron DEAE.

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