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GEL CHROMATOGRAPHY OF RHENIUM(VII)

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SUMMARY

The gel chromatographic behaviour of the perrhenate anion on Sephadex G-10 and Bio-Gel P-2 was investigated. Chelate complex formation was observed on Sephadex at pH values below 3.0. K_d values of about 4.5 were measured in neutral and alkaline solutions. No chelate complex formation occurred on Bio-Gel P-2 within the stability range of this gel. K_d values of 2.6 were found independently of pH variations. The results are compared with those for the behaviour of vanadium(V), molybdenum(VI) and tungsten(VI).

INTRODUCTION

Rhenium(VII), like manganese(VII) and technetium(VII), exists in aqueous solutions in the form of oxo-anions. In contrast to vanadium(V), molybdenum(VI) and tungsten(VI), these oxo-anions do not exhibit any tendency to form isopoly-acids. Hence, it was of interest to investigate whether the behaviour of perrhenate ions on dextran and polyacrylamide gels is analogous to that of vanadate, molybdate and tungstate ions. Those isopoly-acid forming ions were found to exhibit an increasing tendency to form chelate complexes with decreasing pH values[1–3]. Further, isopoly-acid formation also increases with decreasing pH and molecular sieving is the second dominant factor in determining their elution profiles. For tungsten(VI), it was possible clearly to correlate the K_d values of certain isopoly-acid species and their degree of condensation by column chromatography on Sephadex G-10 (ref. 4).

In contrast to permanganate, perrhenate is a much weaker oxidant so that there is no risk of oxidation of dextran and polyacrylamide gels.

EXPERIMENTAL

Apparatus

Home-made Plexiglass columns were used for chromatography. Application of the sample and elution were carried out by means of a 4912 A peristaltic pump from LKB (Bromma, Sweden). An LKB 7000 UltroRac with a drop counter was used to collect the eluted fractions.

A Philips PW 1220/C sequence spectrometer was used for the quantitative X-

ray fluorescence spectrometric determination of rhenium. Measurements were carried out under the following conditions: gold target tube, 50 kV, 40 mA; PVC cells with bottom consisting of 6-μm Mylar foil and with lids; LiF (200) crystal; fine collimator (lamellar spacing 160 μm); counting time 20 or 40 sec; measurement at the Re L_α-line, first order, with proportional and scintillation counter in series; automatic pulse height selection by a sin θ potentiometer for LiF and with a fixed window.

Materials

Sephadex G-10 (fine) was obtained from Pharmacia (Uppsala, Sweden) and 200–400 mesh Bio-Gel P-2 from Bio-Rad Labs. (Richmond, Calif., U.S.A.). Ammonium perrhenate was supplied by H. C. Starck (Goslar, G.F.R.). All other reagents were of analytical reagent grade from Merck (Darmstadt, G.F.R.).

Preparation of perrhenate starting solutions

Ammonium perrhenate (NH_4ReO_4) was dissolved in water. The pH was adjusted with 6 *M* hydrochloric acid in the acid range and by the addition of concentrated ammonia solution in the alkaline range.

Column chromatography

The conditions for the experiments on Sephadex G-10 were as follows: bed dimensions, 10 × 3.0 cm (= 70.7 ml); flow-rate, 14 ml/h·cm² (= 100 ml/h); sample size, 5.0 ml; volume of collected fractions, 5.0 ml; interstitial volume of column, v_0 = 26.7 ml; inner gel volume, v_i = 17.0 ml; room temperature, 19–22°.

The conditions for the experiments on Bio-Gel P-2 were as follows: bed dimensions, 25 × 1.90 cm (= 71 ml); flow-rate, 17.5 ml/h·cm² (= 50 ml/h); sample size, 5.0 ml; volume of collected fractions, 5.0 ml; interstitial volume of column, v_0 = 31.3 ml; calculated total inner gel volume, v_i = 24.5 ml; room temperature, 19–22°.

RESULTS AND DISCUSSION

Tests on Sephadex G-10

The results of the experiments on the sorption of rhenium(VII) on Sephadex G-10 are summarized in Table I. Fig. 1 shows the corresponding elution profiles. Ammonium perrhenate is eluted with considerable delay at pH 10 (K_d = 4.53). Similar elution behaviour of the perchlorate anion, *i.e.*, of an ion with a close structural resemblance to the perrhenate ion, was observed elsewhere[5,6]. Peak elution volumes of sodium sulphate, nitrate, perchlorate and hydroxide increased in this order on a Sephadex G-15 column. Perchlorate and hydroxide exhibited pronounced interactions with the gel matrix, as shown by Langmuir-type elution profiles and exothermic sorption (*i.e.*, high detection sensitivity in a thermal detector)[6]. With perrhenate, however, a slight tendency to form anti-Langmuir-type elution profiles (beard formation) occurred. As with perchlorate, the sorption phenomenon is not yet fully understood. It is apparently insensitive to pH variations, and is probably due to the formation of hydrogen bonds with the hydroxyl groups of the dextran matrix. Hydrogen bonding has also been suggested to be responsible for the retardation of perchlorate ions on polyacrylamide gels[7]. The sorption mechanism is probably identi-

TABLE I

COLUMN CHROMATOGRAPHIC EXPERIMENTS ON THE BEHAVIOUR OF RHENIUM-(VII) ON TIGHTLY CROSS-LINKED GELS

Abbreviations: No. = number of column test; pH = pH of starting solution as well as of the eluent (*e.g.*, pH 2.0, elution with 0.01 *M* HCl): Total recovery = percentage of total amount of rhenium applied (measured up to *x* ml elution volume); Peak, ml = volume region of peak elution. The concentration of ammonium perrhenate solution applied to the column was 0.1 *M* in all instances.

No.	*Gel*	*pH*	*Total recovery*		*Peak*		*Notes*
			%	*ml*	*ml*	K_d	
1	Sephadex	10.0	98	(140)	101–106	4.53	Slight beard formation
2	G-10	6.0	102	(140)	102–107	4.56	Peak practically identical with that of No. 1
3		3.0	101	(190)	106–111	4.83	No beard but tailing
4		2.0	57	(160)	119.5–124.5	5.60	Pronounced sorption
5		1.5	33	(200)	180.5–185.5	9.20	Very distinct sorption
6	Biogel	8.0	92	(120)	93.5–98.5	2.64	Peak perfectly symmetrical
7	P-2	6.0	94	(120)	91.5–96.5	2.56	Peak perfectly symmetrical
8		3.0	95	(120)	94.5–99.5	2.68	Peak perfectly symmetrical

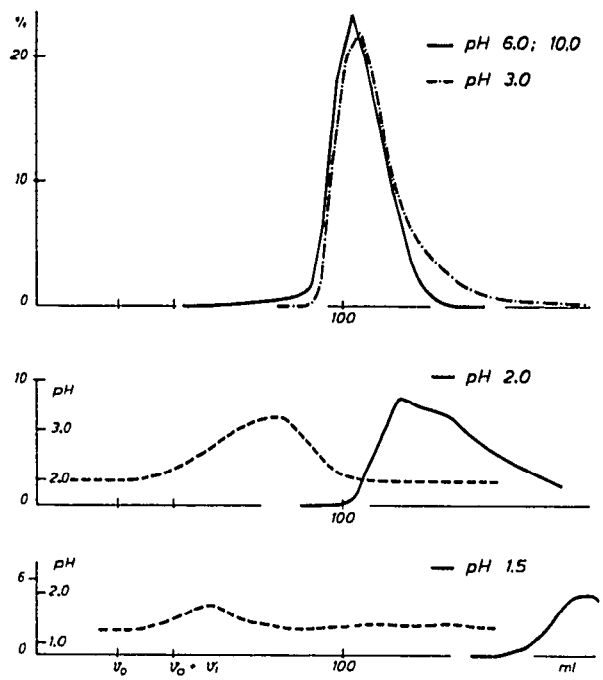

Fig. 1. Elution profiles of 0.1 *M* perrhenate solutions on Sephadex G-10 as a function of pH variations. Ordinate: percentage of total amount of rhenium applied to the column per collected fraction; abscissa: eluate (ml); v_0 = void volume (measured with Dextran 2000); $v_0 + v_i$ = peak elution volume of a substance with unrestricted access to the gel phase. The broken lines in the middle and lower diagram indicate the pH elution profiles with the pH scale on the ordinate.

cal with that which causes the sorption of rhenium(VII) on cellulose and various resins and has also been called "hydrophobic interaction".

With decreasing pH, however, rhenium(VII) exhibits an increasing tendency to form chelate complexes, as has been observed for isopoly-acid forming oxo-anions. Chelate complexation is suggested by the pH elution profiles shown in Fig. 1: the pH increases during complex formation, which leads to a pH maximum after $v_0 + v_t$. In contrast to vanadate, molybdate and tungstate, pronounced chelate complex formation occurs only below pH 2.0.

Tests on Bio-Gel P-2

The tests on Bio-Gel P-2, the results of which are given in Table I, gave symmetrical peaks with K_d values of about 2.6. This value is considerably greater than the K_d values measured for alkali metal perchlorates by Saunders and Pecsok[8] (lithium perchlorate, 1.97; sodium and potassium perchlorate, 1.77). However, they are still in the range of K_d values found for other salts, particularly iodides (barium iodide, 2.61; aluminium iodide, 2.96)[8]. Thus, perrhenate is also strongly retarded on polyacrylamide gels but presumably with linear sorption isotherms and again by hydrogen bonding. In contrast to vanadate, molybdate and tungstate, however, rhenium(VII) does not form chelate complexes on polyacrylamide gels.

CONCLUSION

Metal oxo-anions with and without the tendency to form isopoly-acids seem to form chelate complexes with the hydroxyl groups of the gel matrix of dextran gels. The tendency generally increases with decreasing pH. The complexes are stable in acid media only. They are formed with the release of hydroxyl ions, which can be observed in batch experiments[1,2] as well as by recording pH–elution profiles in column experiments. The tendency for chelate complexation with the dextran matrix to occur increases with the tendency of the different oxo-anions to form isopoly-acids. Both processes are chelate complex formation so that the parallelism of the trends is not surprising. Particularly vanadium(V) and less so molybdenum(VI) and tungsten(VI), exhibit sorption by complex formation in neutral solutions, whereas for rhenium(VII) adsorption occurs only at pH values below 3.0. This can be explained by the necessity for the presence of hydroxyl ligands for chelate complex formation with dextran gels. Vanadium(V), molybdenum(VI) and tungsten(VI) form tetraoxo-species in the alkaline range only, where they exhibit no sorption tendency towards dextran gels either. However, they become increasingly coordinated with hydroxyl ions in the neutral region. Consequently, isopoly-acid formation as well as sorption on dextran gels also starts in this pH range. For rhenium(VII), protonation of ReO_4^- to give $ReO_3(OH)$, $ReO_2(OH)_2^+$, etc., requires an acid medium. Obviously, the process starts at about pH 3.0, below which pH increasing sorption on dextran gels can be observed.

Surprisingly high K_d values were observed for the perrhenate anion on dextran gels in the alkaline range and they appeared to be independent of pH down to pH 3.0. By analogy with the similar perchlorate anion, which also shows pronounced sorption on dextran gels, the effect is probably due to the particular structure of these ions.

As with simple metal ions[9], polyacrylamide gels far exceed dextran gels in their

sorption capacity for Group VA and VIA metals, while Biogel P-2 does not exhibit an especially large sorption tendency towards perrhenate within the stability range of the gel.

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