Separation of tungsten and rhenium on alumina

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Abstract: The conditions for the efficient separation of tungsten(VI) and rhenium (VII) on alumina were established. The distribution coefficients K_d for tungstate and perrhenate anions, as well as the separation factors α ($\alpha = K_{dWO_4^{2-}}/K_d\,ReO_4^-$) were determined using hydrochloric or nitric acid as the aqueous media. A solution of sodium chloride in the pH range 2–6 was also examined. Under all the tested experimental conditions, alumina is a much better adsorbent for tungsten than for rhenium. The obtained results indicated that the best separation of these two elements is achieved when 0.01– 0.1 mol dm^{-3} HCl or 1.0 mol dm^{-3} HNO$_3$ are used as the aqueous media. If NaCl is used as the aqueous phase, the best separation is achieved with 0.20 mol dm^{-3} NaCl, pH 4–6. Under these experimental conditions, the breakthrough and saturation capacities of alumina for tungsten at pH 4 are 17 and 26 mg W/g Al$_2$O$_3$, respectively. With increasing pH, these values decrease. Thus, at pH 6 they are only 4 and 13 mg W/g Al$_2$O$_3$, respectively.

Keywords: tungsten, rhenium, separation factor, distribution coefficient.

INTRODUCTION

In recent years particular emphasis has been devoted to the radioisotope ^{188}Re, which is potentially very interesting for applications in nuclear medical therapy. Rhenium-188 ($T_{1/2}$ = 17 h) is the decay product of its parent ^{188}W ($T_{1/2}$ = 69 d) which is formed in a nuclear reactor during irradiation of tungsten targets. However, the isolation of rhenium from tungsten is not simple.

For the separation of these two elements, several procedures have been proposed, such as, *e.g.*, solvent extraction with methyl ethyl ketone[1] or pyridine.[2] After evaporation of the organic phase, the resultant residue is disolved in NaCl. By a similar extraction procedure, rhenium is separated by precipitation as tetraphenylarsonium perrhenate or rhenium sulphide.[3] The main drawback of these procedures is the rather poor efficiency. Hence, an additional purification step is often needed. Adsorption studies for W and Re were performed using anion exchangers

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and different aqueous media.[4,5] It was reported that tungsten is strongly sorbed from weakly acidic and basic solution on activated carbon[6] or ZrO_2.[7] Rhenium is adsorbed to a much lesser extent and can be eluted by distilled water. However, the yields are rather low. Many studies have been devoted to the development of an efficient routine separation procedure based on alumina as the adsorbent.[4,8]

EXPERIMENTAL

Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, Fluka) and potassium perrhenate ($KReO_4$, Aldrich) were commercialy p.a. grade chemicals. The adsorbent was alumina for column chromatography (Alumina N- Super I, ICN Biomedicals).

The bulk solutions were prepared by dissolution of $Na_2WO_4 \cdot 2H_2O$ and $KReO_4$ in bidistilled water. The final concentrations of tungsten and rhenium in the corresponding aqueous media were 5.4×10^{-3} mol dm^{-3} and 5.3×10^{-3} mol dm^{-3}, respectively.

As the aqueous media, solutions of HCl or HNO_3 of differing concentrations (0.001, 0.01, 0.1 and 1.0 mol dm^{-3}) were prepared. The concentrations of NaCl solution were 0.06, 0.12, 0.15 and 0.20 mol dm^{-3} in the pH range 2–6 (± 0.2). The desired pH was adjusted by HCl. Only freshly prepared solutions were used for the experiments.

Alumina, grain size 40–140 μm, was used without any pretreatment.

The concentrations of tungsten and rhenium in the solutions were determined by direct current argon arc plasma atomic emission spectroscopy (DCP-AES) with an aerosol supply. A U-shaped DC arc was used as the excitation source and a 2-meter plane grating spectrograph PGS-2 (Carl-Zeiss) with a self-made attachment for photoelectric detection was used as the monochromator. A Bausch and Lomb echelle grating with 316 grooves/mm, blaze angle 63º 26 and order sorter were used. Using a Babington type nebulizer supported by a peristaltic pump, the solutions were sprayed into the plasma. Potassium as a spectrochemical buffer, was added to all samples to give a final concentration of 6.7×10^{-2} mol dm^{-3} KCl.[9,10]

For rhenium, the most sensitive atomic line ReI 346.047 nm was used (limit of detection LOD = 1×10^{-7} mol dm^{-3}). For tungsten, the atomic line WI 400.88 nm was used (LOD = 5.4×10^{-7} mol dm^{-3}).

The determination of the distribution coefficients was carried out by equilibrating 0.20 g of Al_2O_3 in 40 ml of the corresponding aqueous medium for 2 h. Then, the sorbent was separated from the solution by centrifugation (3000 rpm, 20 min; Beckman, Model J-6B). The amount of the element bound to Al_2O_3 was determined from the difference in the concentrations in the solution before and after equilibration.

The distribution coefficient K_d is given by:

$$K_d = (1-x)V/xm$$

where x – is the experimentally determined fraction of the given element remaining in the solution, V – the volume of the aqueous phase, ml, $1-x$ – the fraction of the given element bound to alumina and m – amount of alumina used, g.

From distribution coefficients K_d, the separation factors α ($\alpha = K_{dWO_4^{2-}}/K_d ReO_4^-$) were calculated.

Column experiments were performed for the system: alumina – 0.20 mol dm^{-3} NaCl, pH 2–6. Before use, the columns wee conditioned with the appropriate aqueous phase. The efluent was collected in 1 ml fractions.

The breakthrough and saturation capacities of alumina for W(VI) were determined in a glass column (8 mm diameter; 40 mm length) containing 1 g of Al_2O_3. The concentration of tungsten was 5.4×10^{-3} mol dm^{-3} in 0.20 mol dm^{-3} NaCl, pH 2–6 ($\pm$ 0.2). The flow rate was 2.5 ml $min^{-1}cm^{-2}$.

The values of the distribution coefficients suggest that the capacity of alumina for rhenium is low. Therefore its breakthrough and saturation capacities were not determined.

The elution volumes of rhenium, in dependance on the pH of the eluent, were determined in a glass column (10 mm diameter; 100 mm length) containign 3.5 g Al_2O_3. After sorption of 1 ml of rhenium solution (9×10^{-3} mol dm^{-3} in 0.2 mol dm^{-3} NaCl), the rhenium was eluted by 0.20 mol dm^{-3} NaCl, pH 2–6 ($\pm$ 02.). The flow rate of the eluent solution was 1.5 ml min^{-1}cm^{-2}. The elution volume was the volume of the corresponding NaCl solution required for the elution of more than 98 % of rhenium.

Under the given experimental conditions, tungsten is efficiently adsorbed on alumina. Therefore, the elution volumes for tungsten were not determined.

All analyses were conducted at room temperature (22 ± 2 ºC) and in duplicate. If the discrepancy was more than 10 %, one more experiment was made. The mean values are given in the Tables.

RESULTS AND DISCUSSION

Sorption studies of WO_4^{2-} and ReO_4^- were performed using alumina and solutions of hydrochloric or nitric acid. The distribution coefficients K_d of these two elements were determined over a wide range of concentrations of the aqueous phase (0.001–1.0 mol dm^{-3}). The separation factors α, given as $\alpha = K_{dWO4}{}^{2-}/K_{dReO4}{}^-$, representing the separation feasibility of these two elements, were calculated. The variations of K_d and α values in dependance on the concentration of HCl and HNO$_3$ are given in Table I.

It can be seen that, in the case of HCl as the aqueous phase, alumina exhibits much higher affinity towards WO_4^{2-} than ReO_4^- throughout the examined concentration range. The K_d values for W(VI) first increase and then decrease with increasing acid molarity and are always much higher than those for rhenium. Under the same experimental conditions, the K_d values for Re(VII) decrease with increasing acid molarity.

The highest values of the separation factor α were obtained when HCl in the concentration range 0.01–0.1 mol dm^{-3} was used.

When nitric acid was used as the aqueous medium, the tungstate and perrhenate anions behave in a similar manner. Generally, the values of K_d for tungsten are lower but still much higher than the K_d values for Re(VII). For rhenium, both in HCl and HNO$_3$, no significant differences in the K_d values were observed.

TABLE I. Dependance of the distribution coefficients K_d for tungstate and perrhenate anions and the distribution factors α ($\alpha = K_{d\ WO4}{}^{2-}/K_{d\ ReO4}{}^-$) on the concentrations of hydrochloric and nitric acid: $c_W = 5.4\times10^{-3}$ mol dm^{-3}; $c_{Re} = 5.3\times10^{-3}$ mol dm^{-3}

Acid	Coefficient	Concentration of the acid/mol dm^{-3}			
		0.001	0.01	0.1	1.0
HCl	$K_{d\ WO4}{}^{2-}$	5600	47000	46000	13000
	$K_{d\ ReO4}{}^-$	65	20	10	9
	α	86	2350	4600	1440
HNO$_3$	$K_{d\ WO4}{}^{2-}$	1900	20000	1100	17000
	$K_{d\ ReO4}{}^-$	50	20	14	15
	α	38	1000	78	1130

The highest values of α were obtained when 1 mol dm^{-3} HNO$_3$ was used.

The results obtained when NaCl was used as the aqueous phase are shown in Table II.

TABLE II. Dependence of the distribution coefficients K_d for tungstate and perrhenate anions and the distribution factors α ($\alpha = K_{d\ WO4}{}^{2-}/K_{d\ ReO4}{}^-$) on the concentration and pH of sodium chloride solutions: $c_W = 5.4\times10^{-3}$ mol dm^{-3}; $c_{Re} = 5.3\times10^{-3}$ mol dm^{-3}

NaCl/mol dm^{-3}	Coefficient	pH		
		2 ± 0.2	4 ± 0.2	6 ± 0.2
0.06	$K_{d\ W}$	13000	2300	370
	$K_{d\ Re}$	20	1.6	5.4
	α	650	1438	68.5
0.12	$K_{d\ W}$	55000	600	130
	$K_{d\ Re}$	50	25	6
	α	1100	24	22
0.15	$K_{d\ W}$	18000	800	120
	$K_{d\ Re}$	20	3	5
	α	900	270	24
0.20	$K_{d\ W}$	11000	800	100
	$K_{d\ Re}$	20	0.1	< 0.1
	α	550	8000	> 1000

The results presented in Table II reveal that the K_d values for both tungsten and rhenium decrease with increasing pH for all the examined NaCl concentrations. Similarly, as in the case of HCl and HNO$_3$, the values of K_d for W(VI) were much higher than those for Re(VII). This means that, also under these experimental conditions, alumina adsorb W(VI) much more readily than Re(VII).

The best separation of WO$_4$$^{2-}$ and ReO$_4$$^-$ can be achieved when NaCl of higher concentration (0.20 mol dm^{-3}) is used. The highest values for α are at pH 4–6. However, it can be seen that this is primarily due to lower K_d values for rhenium and not to high values of K_d for tungsten.

According to the results presented in Tables I and II, favorably high values of K_d and α are obtained with the following systems:

1. Alumina–HCl (0.01–0.1 mol dm^{-3})
2. Alumina–HNO$_3$ (1.0 mol dm^{-3})
3. Alumina–NaCl (0.20 mol dm^{-3}; pH 4–6)

From the practical point of view, despite good possibilities of separating tungsten and rhenium, the use of even dilute mineral acids has disadvantages which should be considered. The disadvantage of the use of mineral acids is that they are,

in most cases, incompatible with the intended application of the separated rhenium. In these cases, the adequate aqueous medium would be a NaCl solution.

The breakthrough and saturation capacities of alumina for tungstate anion and the elution volumes for rhenium are shown in Table III.

TABLE III. Breakthrough and saturation capacities of alumina for tungsten(VI) and the elution volumes of rhenium(VII). Column: 10 mm diameter, 100 mm length; Bed: 3.5 g Al_2O_3 N Super I (ICN Biomedicals)

pH of 0.20 mol dm^{-3} NaCl	Breakthrough capacity mg W/g Al_2O_3	Saturation capacity mg W/g Al_2O_3	Elution volume of ReO_4^-/ml
6	4	13	15
4	17	26	15
2	24	78	16

The data in Table III present the adsorption characteristics of alumina when the aqueous phase was 0.20 mol dm^{-3} NaCl. The capacities depend on pH. The breakthrough capacity decreases with increasing pH, *i.e.*, instead of being 17 mg W/g A_2O_3 at pH 4, it is only 4 mgW/g Al_2O_3 at pH 6. Similar trends were also observed for the saturation capacities.

The results for the elution volumes of rhenium refer to the applied experimental conditions. It can be concluded that, for the given column dimensions (10 mm diameter, 100 mm length) and the used quantity of the adsorbent (3.5 g Al_2O_3N Super, I, ICN Biomedicals), the volume of 0.20 mol dm^{-3} NaCl necessarry for the elution of rhenium does not depend on pH. It is about 15 ml throughout the examined pH range.

CONCLUSION

Sorption studies for WO_4^{2-} and ReO_4^- were carried out using alumina and aqueous solutions of HCl, HNO_3 and NaCl of different concentrations. The distribution coefficients K_d were determined. The separation factors α, given as $\alpha = K_d WO_4^-/K_d ReO_4^-$, representing the separation feasibility of these two anions, were calculated.

The experiments confirmed that alumina is, under all examined experimental conditions, a much better adsorbent for tungstate than for perrhenate anions. Good separation can be achieved in the aqueous media containing either 0.01–0.1 mol dm^{-3} HCl or 1.0 mol dm^{-3} HNO_3.

The system alumina–0.20 mol dm^{-3} NaCl (pH 4–6) was found to be suitable because of the high separation factor α, low concentration of NaCl and very small values of K_{dReO4}^-. The breakthrough and saturation capacities of alumina for tungsten are relatively high. For the given column and the used quantity of alumina, it was found that rhenium can be separated with a relatively small volume of NaCl solution.

ИЗВОД

РАЗДВАЈАЊЕ ВОЛФРАМА И РЕНИЈУМА НА АЛУМИНИЈУМ-ОКСИДУ

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Испитани су услови за ефикасно раздвајање волфрама(VI) и ренијума(VII) на Al_2O_3. Одређени су коефицијенти дистрибуције K_d као и фактори сепарације α ($\alpha = K_d$ $_{WO4}{}^{2-}/K_d$ ReO_4^-) када се као водена фаза користе HCl или HNO_3. Такође је као водена фаза узет и раствор NaCl у области pH 2–6. Под свим проучаваним експерименталним условима, Al_2O_3 је много бољи адсорбенс за волфрам него за ренијум. Упоређивањем добијених резултата може се закључити да се најбоља сепарација ова два елемента постиже када се као водена фаза користе 0,01–0,1 mol dm^{-3} HCl или 1,0 mol dm^{-3} HNO_3. Најбоља сепарација са раствором NaCl добија се са 0,20 mol dm^{-3} NaCl у опсегу pH 4–6. Под овим експерименталним условима, пробојни и сатурациони капацитети Al_2O_3 за волфрам на pH 4, износе 17 односно 26 mg W/g Al_2O_3. Са порастом pH, ове вредности се смањују. Тако, при pH 6, оне износе још само 4 mg W/g Al_2O_3 за пробојни и 13 mg W/g Al_2O_3 за сатурациони капацитет.

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