Sorption of rhenium on alumina under dynamic conditions

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Abstract: The sorption of perrhenate anion on alumina from aqueous solutions of sodium chloride was investigated under dynamic conditions. The initial concentrations of rhenium were in the range of 2.7×10^{-2}–2.7 mmol/dm^3. The breakthrough curves as the function of Re and NaCl concentrations (0.12–0.20 mol/dm^3), pH 2–6 and flow rate 3–10 ml/min were determined. According to the experimental results, it was concluded that the breakthrough capacities, the capacities at $c/c_0 = 0.5$, the total column capacities and the utilization degrees (column efficiency) increase with increasing Re and NaCl concentrations and decreasing pH. The optimal flow rate was found to be 3 ml/min. At pH 2 and $c_0 = 2.7$ mmol Re/dm^3, the total capacity was found to be $Q_{0.9}{}^{max} = 2.1 \times 10^{-2}$ mmol Re/g Al$_2$O$_3$. The data for perrhenate anions fit with a Henry-type isotherm. It was found that, under the above mentioned conditions, the value of the Henry constant K_H was 7.8×10^{-3} dm^3/g and the Gibbs energy change, ΔG was –0.5 kJ/mol.

Keywords: rhenium, sorption, alumina, sorption capacity, sorption isotherm.

INTRODUCTION

Several radioisotopes find use in nuclear medicine. While in diagnostics, technetium-99m (^{99}Tc) is predominant,[1] in therapy several radioistopes are considered. Among them an important place is reserved for the radioisotopes of rhenium – namely ^{186}Re and ^{188}Re.[2] They are beta emitters with half-lives of 3.71 d and 17 h, respectively. They can be obtained by direct neutron activation using the (n,γ) nuclear reaction but only low specific activity can be produced.[3] An important advantage of ^{188}Re is that it can be produced from a ^{188}W/^{188}Re radionuclidic generator.[4] In this case, the daughter ^{188}Re is obtained in a carrier-free form suitable for labeling of currently very modern radiopharmaceuticals– monoclonal antibodies (MoAb), peptides, *etc.*

The generator ^{188}W/^{188}Re has been intensively investigated. For its development and optimization, a detailed investigation of sorption processes was required.

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The main parameters regarding the sorption of both anions on alumina in the batch technique were examined.[5] The conditions for the sorption of tungsten on alumina under dynamic conditions were also determined.[6] The current paper deals with the sorption of the perrhenate anion under similar experimental conditions.

EXPERIMENTAL

All chemicals were of reagent grade. Potassium rhenate, $KReO_4$, (Aldrich) was dissolved in warm bidistilled water. Alumina for the column chromatography (Alumina N-super I, ICN Biomedicals), grain size 40–140 μm, was used without pretreatment.

The concentration of rhenium in the solution was determined by direct current argon arc plasma atomic emission spectroscopy (DCP-AES) with an aerosol supply. A U-shaped DC are was used as the excitation source and a 2-meter plane grating spectrograph PGS-2 (Carl–Zeiss) with a laboratory-made attachment for photoelectric detection was used as the monochromator. A Bausch and Lomb echelle grating with 316 grooves/min, angle blaze 63°26 and an order sorter were used. Using a Babingon-type nebulizer supported by a peristaltic pump, the solutions were sprayed into the plasma. Potassium, as the spectrochemical buffer, was added in all samples to a final concentration of 67 mmol KCl/1.[7,8]

For rhenium, the most sensitive atomic line ReI 346.05 nm was used. The limit of detection, LOD, was 1.0×10^{-7} mol dm^{-3}.

The experiments were performed in a glass column of 8 mm internal diameter. For each experiment, the column was filled with 1.0 g Al_2O_3. The height of the sorbent layer was 2.8 cm and its volume 1.4 ml. To avodi air bubbles, the alumina was carefully packed undere distilled water. Prior to the experiment, the sorbent was washed with the corresponding NaCl solution. Constant flow rates of the solution through the column were achieved using a Masterflex C/L pump (Cole-Palmer Instrument Company). In the sorption experiments, the concentrations of rhenium were 2.7×10^{-2}, 5.4×10^{-2}, 2.7×10^{-1} and 2.7 mmol/l, while the concentrations of NaCl solution were 0.12, 0.15 and 0.20 mol/l. The pH values were 2, 4 and 6 (±0.2). The desired pH was adjusted using dilute HCl. For the experiments, only freshly prepared solutions were used. The flow rates of the solution in the downward direction were 3, 5 and 10 ml/min. The samples of the initial solutions and of the successive fractions (5 ml) were taken for the chemical analyses.

The experiments were conducted at room temperature (22±2 °C).

RESULTS AND DISCUSSION

The sorption of rhenium on alumina under dynamic conditions depends on the Re and NaCl concentrations, pH and flow rate.

The breakthrough curves of perrhenate anions on alumina were determined as a function of the Re and NaCl concentrations, pH and flow rates. A typical example of the results obtained for various flow rates (3–10 ml/min), at constant initial rhenium (2.7×10^{-2} mmol/l) and NaCl (0.15 mol/l) concentrations and pH 4, is shown in Fig. 1.

As can be seen from Fig. 1, variation of the flow rates (3, 5 and 10 ml/min) did not influence the rhenium sorption at pH 4. The same results were also obtained at pH 2 and pH 6. This means that the applied flow rates did not affect the sorption, *i.e.*, no significant difference in the amount of sorbed rhenium was observed. The sorption occurred under dynamic equillibrium conditions. All further experiments were performed with a flow rate of 3 ml/min.
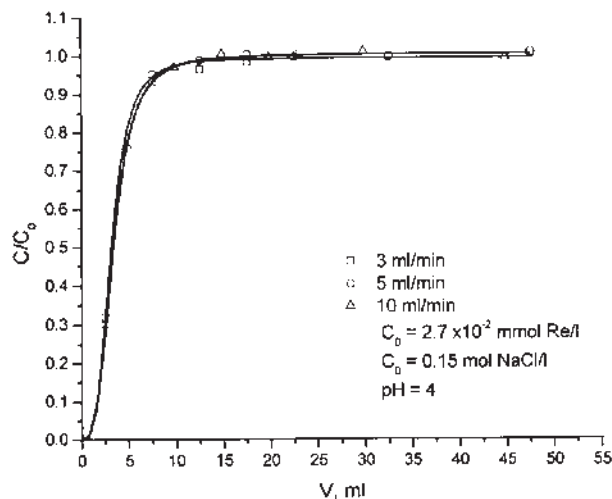
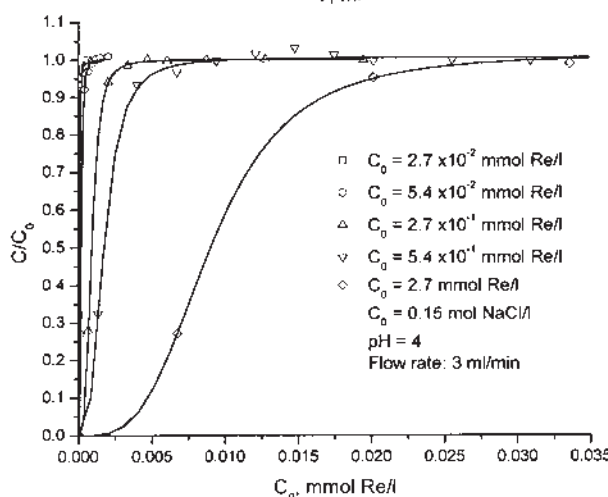Fig. 1. Breakthrough curves of perrhenate anions on alumina in dependence on the flow rate.

Fig. 2. Breakthrough curves of perrhenate on alumina in dependence on the initial rhenium concentration.

It can also be concluded that the shape of the brekthrough curves does not depend on the flow rate. It can be supposed that under the given experimental conditions, the mass transfer coefficient remains unchanged.

Figure 2 presents the breakthrough curves obtained in dependence on the rhenium concentrations (2.7×10^{-2} – 2.7 mmol/l). The flow rate was kept at 3 ml/min and the pH at 4.

From Fig. 2 it can be seen that the sorption efficiency increases with increasing initial rhenium concentration. However, the shape of the breakthrough curves in this case also remains unaffected.

The dependence of the breakthrough curves on the concentration of NaCl solution (ionic strength) is shown in Fig. 3. Other parameters (rhenium concentration, flow rate and pH) were kept constant. As in the previous Figures, it can be seen that the curves exhibit a symetrical shape.
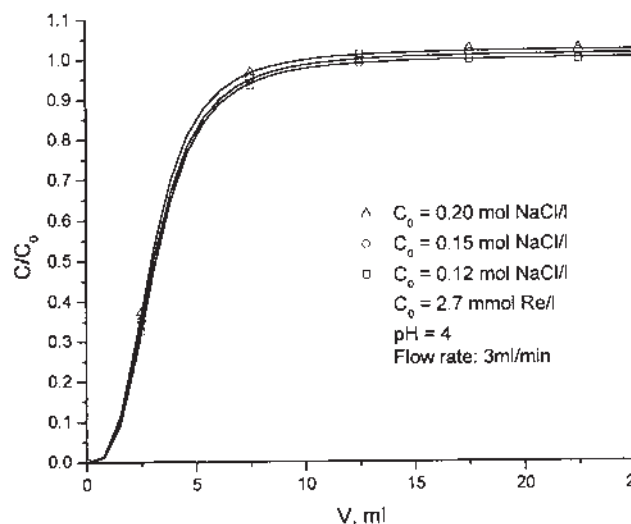
Fig. 3. Breakthrough curves of perrhenate on alumina in dependence on the NaCl concentration.

For the given set of experimental conditions, the linear flow rates, designated also as the superficial velocities, u, were calculated. The values, for the flow rates 3, 5 and 10 ml/min are 6, 10 and 20 cm/min, respectively.

The main residence or contact time (τ_c) between the solution and the sorbent can be calculated by:[9]

$$\tau_c = \varepsilon l/u \qquad (1)$$

where: ε is the extraparticle bed porosity or void fraction of the sorbent bed (for alumina the calculated value $\varepsilon \approx 0.33$), l is the bed height of the sorbent (in the experiments $l = 2.8$ cm) and u is the linear or interstitial velocity (cm/s).

For the value of $u = 6$ cm/min (*i.e.,* a flow rate 3 ml/min), the calculated contact time $\tau_c = 0.16$ min, *i.e.,* 9.6 s.

From the experimental results, the values of the breakthrough capacity ($Q_{0.05}$), the capacity at $c/c_0 = 0.5$ ($Q_{0.5}$), the total column sorption capacity (Q) and the utilization degree or the column efficiency (E) were calculated. According to the literature,[10,11] the breakthrough point can be determined as the point at which the concentration of rhenium in the effluent solution reaches 5 % of the rhenium concentration in the influent solution. The exhaustion point of the column could, theoretically, be achieved either after infinite time or by using an infinite effluent volume. Therefore, for practical reasons, the total column sorption capacity is calculated from the area left of the point at which the breakthrough curve reaches the value of $c/c_0 = 0.9$. The values for the columns efficiency, E, are obtained as the ratio of the breakthrough capacity to the total column sorption capacity.

The dependence of Q and E values of pH (2–6) and NaCl concentrations (0.12–0.20 mol/l) are given in Table I. The concentration of rhenium (2.7 mmol/l) and the flow rate (3 ml/min) were kept constant.

TABLE I. The $Q_{0.05}$, $Q_{0.5}$, $Q_{0.9}$ and E values in dependence on pH (2–6) and NaCl concentration at $c_0 = 2.7$ mmol Re/l and a flow rate of 3 ml/min

NaCl/mol^{-1}	pH	$Q_{0.9}$/(mmol Re/g Al$_2$O$_3$)	$Q_{0.5}$/(mmol Re/g Al$_2$O$_3$)	$Q_{0.05}$/(mmol Re/g Al$_2$O$_3$)	E/%
0.20	2	2.2×10^{-2}	1.0×10^{-2}	1.8×10^{-3}	8.0
	4	1.9×10^{-2}	9.5×10^{-3}	1.6×10^{-3}	8.5
	6	1.8×10^{-2}	8.6×10^{-3}	1.4×10^{-3}	8.1
0.15	2	2.1×10^{-2}	9.7×10^{-3}	1.3×10^{-3}	7.7
	4	1.7×10^{-2}	9.1×10^{-3}	1.3×10^{-3}	8.1
	6	1.6×10^{-2}	8.5×10^{-3}	1.1×10^{-3}	6.6
0.12	2	1.9×10^{-2}	9.5×10^{-3}	1.3×10^{-3}	6.9
	4	1.7×10^{-2}	8.5×10^{-3}	1.1×10^{-3}	6.2
	6	1.7×10^{-2}	8.3×10^{-3}	8.6×10^{-4}	5.1

The dependence of Q and E values on the rhenium concentration is shown in Table II. The NaCl concentration (0.15 mol/l) and the flow rate (3 ml/min) were kept constant.

TABLE II. The dependence of $Q_{0.9}$, $Q_{0.5}$, $Q_{0.05}$ and E values on the rhenium concentration and pH ($c_{NaCl} = 0.15$ mol/l; 3 ml/min)

pH	c_0/(mmol Re/l)	$Q_{-0.9}$/(mmol Re/g Al$_2$O$_3$)	$Q_{0.5}$/(mmol Re/g Al$_2$O$_3$)	$Q_{0.05}$/(mmol Re/g Al$_2$O$_3$)	E/%
2	$2.7. \times 10^{-2}$	2.1×10^{-4}	9.1×10^{-5}	3.0×10^{-5}	14.0
	5.4×10^{-2}	4.5×10^{-4}	2.1×10^{-4}	7.8×10^{-5}	17.5
	2.7×10^{-1}	2.3×10^{-3}	1.0×10^{-3}	3.2×10^{-4}	14.0
	5.4×10^{-1}	4.2×10^{-3}	2.1×10^{-3}	5.4×10^{-4}	12.8
	2.7	2.1×10^{-2}	9.7×10^{-3}	1.1×10^{-3}	5.1
4	2.7×10^{-2}	1.7×10^{-4}	8.4×10^{-5}	2.0×10^{-5}	11.7
	5.4×10^{-2}	3.7×10^{-4}	1.8×10^{-4}	7.2×10^{-5}	19.3
	2.7×10^{-1}	1.7×10^{-3}	8.9×10^{-4}	2.6×10^{-4}	15.5
	5.4×10^{-1}	3.8×10^{-3}	1.9×10^{-3}	4.6×10^{-4}	12.3
	2.7	1.7×10^{-2}	9.1×10^{-3}	1.3×10^{-3}	8.1
6	2.7×10^{-2}	1.4×10^{-4}	7.9×10^{-5}	1.0×10^{-5}	7.2
	5.4×10^{-2}	3.2×10^{-4}	1.7×10^{-4}	2.7×10^{-5}	8.6
	2.7×10^{-1}	1.6×10^{-3}	8.3×10^{-4}	2.2×10^{-4}	13.3
	5.4×10^{-1}	3.6×10^{-3}	1.8×10^{-3}	3.7×10^{-4}	10.2
	2.7	1.6×10^{-2}	8.6×10^{-3}	1.1×10^{-3}	6.6

In can be concluded that the sorption capacity of alumina for perrhenate anions increases with decreasing pH. The highest Q values were obtained at pH 2. The same conclusion can be derived from the data for both the NaCl (Table I) and rhenium (Table II) concentrations.
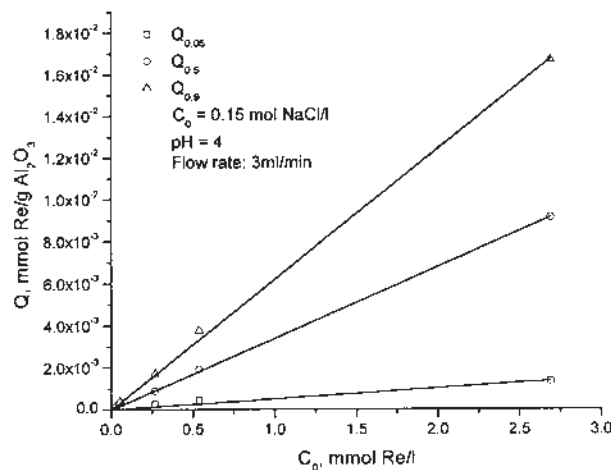
Fig. 4. Sorption isotherms for per-rhenate anions on alumina at c_{NaCl} = 0.15 mol/l at a flow rate of 3 ml/min.

According to the data given in Table II, sorption isotherms were constructed. An example of the dependence of $Q_{0.05}$, $Q_{0.5}$ and $Q_{0.9}$ values on the initial rhenium concentration at pH 4 and a flow rate of 3 ml/min is shown in Fig. 4.

As can be seen, the dependence of $Q_{0.05}$, $Q_{0.5}$ and $Q_{0.9}$ values on the initial rhenium concentration are of linear shape corresponding to a Henry sorption isotherm, given as:

$$Q = K_H c_0 \tag{2}$$

where: K_H is the Henry contant (dm^3/g) which can be determined from the slope. According to the obtained values for K_H, the sorption efficiency of perrhenate anions on alumina can be deduced.

Knowing the K_H values, the Gibbs energy change of rhenium sorption on alumina can be calculated according to:[12]
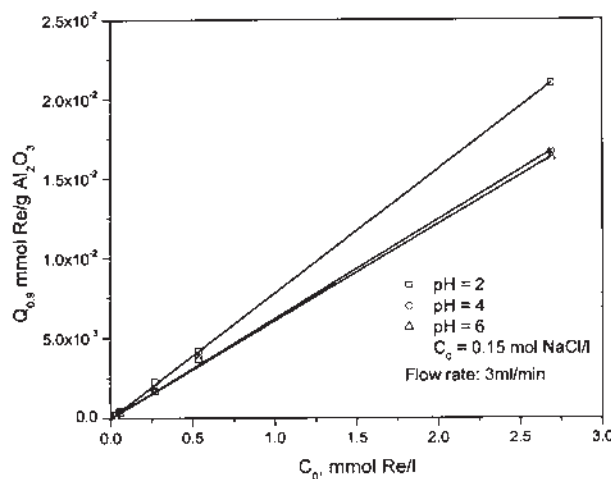

Fig. 5. The dependence of the total sorption capacities ($Q_{0.9}$) on pH (c_0 = 0.15 NaCl mol/l, flow rate 3 ml/min).

$$\Delta G = -RT \ln K_{\text{H}} \qquad (3)$$

where: R is the gas constant, 8.314 J/mol K, and T is the temperature, K. The K_{H} value in Eq. (3) must be dimensionless because the term RT is given in unit J/mol.[13] Since the sorption of perrhenate anions was studied using aqueous solutions containing very low concentrations of anions, K_{H} given in dm^3/g can be easily recalculated in dimensionless values by multiplying the K_{H} values by 1000 (1 dm^3 = 1000 ml or g, since the solution density is $\approx$ equal to1 g/ml).[13]

The calculated values for K_{H} and ΔG and the corresponding regression coefficients are given in Table III.

TABLE III. The values of Henry constant, regression coefficients and ΔG at $c_0 = 0.15$ mol NaCl/l at a flow rate of 3 ml/min

pH	Isotherm	R	K_{H}/(dm^3/g)	K_{H} [1]	ΔG/(kJ/mol)
2	$Q_{0.05} = f(c_0)$	0.9627	6.2×10^{-4}	0.62	1.2
	$Q_{0.5} = f(c_0)$	0.9993	3.6×10^{-3}	3.6	−3.1
	$Q_{0.9} = f(c_0)$	0.9999	7.8×10^{-3}	7.8	−5.0
4	$Q_{0.05} = f(c_0)$	0.9603	5.2×10^{-4}	0.52	1.6
	$Q_{0.5} = f(c_0)$	0.9998	3.4×10^{-3}	3.4	−3.0
	$Q_{0.9} = f(c_0)$	0.9991	6.2×10^{-3}	6.2	−4.5
6	$Q_{0.05} = f(c_0)$	0.9589	4.1×10^{-4}	0.41	2.2
	$Q_{0.5} = f(c_0)$	0.9998	3.2×10^{-3}	3.2	−2.8
	$Q_{0.9} = f(c_0)$	0.9992	6.1×10^{-3}	6.1	−4.4

The dependence of the total sorption capacities ($Q_{0.9}$) of pH for the given experimental conditions ($c_0 = 0.15$ mol/l, flow rate 3 ml/min) is shown in Fig. 5.

The sorption of rhenium on alumina decreases with increasing pH. The best results are obtained at pH 2. In this case, the value of $\Delta G = -5.0$ kJ/mol indicates that, under the given experimental condition the sorption of perrhenate anions on alumina is spontaneous.

CONCLUSIONS

The sorption of perrhenate anions on alumina from aqueous solutions of NaCl was investigated under dynamic conditions in dependence on the Re and NaCl concentrations, pH and flow rate. The sorption was performed under dynamic equilibrium conditions at a solution flow rate of 3 ml/min. The values of the breakthrough capacities, the capacities at $c/c_0 = 0.5$, the total sorption capacities and the utilization degrees of the column increase with increasing Re and NaCl concentrations. The obtained sorption data fit a Henry-type isotherm. It was found that at pH 2 and $c_0 = 2.7$ mmol Re/l, the total capacity $Q_{0.9}^{\text{max}}$ is 2.1×10^{-2} mmol Re/g Al_2O_3. The value of Henry constant $K_{\text{H}} = 7.8 \times 10^{-3}$ dm^3/g. The Gibbs energy change of

rhenium sorption $\Delta G = -5.0$ kJ/mol. This indicates that under these experimental conditions, the sorption of perrhenate anions on alumina is spontaneous.

И З В О Д

СОРПЦИЈА РЕНИЈУМА НА АЛУМИНИЈУМ ОКСИДУ У ДИНАМИЧКИМ УСЛОВИМА

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Испитивана је сорпција перенатног анјона из раствора NaCl на Al_2O_3 у динамичким условима. Почетне концентрације ренијума су биле у опсегу $2,7×10^{-2} - 2,7$ mmol/dm^3. Пробојне криве одређене су у зависности од концентрација ренијума и NaCl ($0,12 - 0,20$ mol/dm^3, pH 2–6 и брзине протока раствора $3 - 10$ ml/min. На основу добијених резултата закључено је да вредности пробојних капацитета, капацитета при $c/c_0 = 0,5$, укупног капацитета колоне и ефикасности колоне расту са порастом концентрација Re и NaCl и опадањем вредности pH. Нађено је да је оптимална брзина протока 3 ml/min. Укупни капацитет на pH 2 и $c_0 = 2,7$ mmol Re/dm^3 износи $Q_{0,9}^{max} = 2,1×10^{-2}$ mmol Re/g Al_2O_3. Добијени подаци одговарају Хенријевом типу изотерме. Нађено је да је, под горе наведеним условима, вредност Хенријеве константе $K_H = 7,8×10^{-3}$ dm^3/g, а вредност промене Гибсове енергије процеса сорпције, $\Delta G = -5,0$ kJ/mol.

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