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THE ION-EXCHANGE BEHAVIOUR OF ARSENIC(III) ON VARION ANION-EXCHANGE RESINS

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SUMMARY

The ion-exchange equilibrium of arsenic ions was studied on the strongly basic anion-exchange resins VARION AD, VARION AT-4 and VARION AT-6. The apparent equilibrium constants (K^x) and the distribution coefficients (D) were determined between the resin and the liquid phases in acidic and alkaline solutions. The effect of arsenic concentration on the course of chromatographic experiments was studied in terms of the breakthrough capacity of the ion-exchange column and the pH of the effluent. VARION AT-6 resin proved to be the most suitable for removing arsenic from highly alkaline solution.

INTRODUCTION

It is well known that arsenic is a very poisonous material, and therefore arsenic compounds from industrial processes must not be allowed to contaminate the waste water. There are a few industrial processes in which arsenic occurs in large amounts and in these cases it would be preferable to remove it from the by-products or the waste water and to recycle it into the process. By that means two problems could be solved: (1) removal of the arsenic, and (2) recycling it for economic reasons. In this paper, experiments are described in which arsenic in alkaline solutions was removed with the aid of ion-exchange resins and, after elution, recirculated into the initial industrial process.

EXPERIMENTAL

VARION AD, VARION AT-4 and VARION AT-6 anion-exchange resins with a polystyrene matrix, produced by Nitrokémia Works (Balatonfüzfő, Hungary) were used. The functional group of VARION AD resin is R_4N^+ Alkanol¹, and of the VARION AT resins it is $R(CH_3)_3N^+$, where R is an alkyl group; the numbers 4 and 6 refer to the degree of cross-linking, VARION AT-4 having a looser lattice. These resins have a high affinity for silicate and carbon dioxide. The silicate binding power of resin VARION AD is below that of the VARION AT types¹.

The resins were used in the Cl^- , SO_4^{2-} , HCO_3^- and OH^- forms. In the equi-

librium systems (*i.e.*, in the batch systems), they were used in a dry form, being dried to constant weight in an oven at 60°.

The arsenic(III) solutions were prepared by dissolving arsenic(III) oxide in 1 *M* potassium hydroxide solution; in other cases, the solutions were taken from the waste water of a factory. Demineralized water was used throughout. The liquid phase was labelled with the isotope ⁷⁶As. The sorption of arsenic was checked by measuring the specific activity of the solutions.

In the equilibrium experiments, 3 g of dried resin and 10 cm³ of the solution were used in each case, at pH values of 4.6 and 7.9. Hydrochloric acid and gaseous carbon dioxide were used to adjust the pH of the solutions.

The equilibrium samples were shaken for 24 h at ambient temperature (22–23°). According to our preliminary experiments, the systems examined attained ion-exchange equilibrium during this time. Then 1–2-cm³ volumes were removed from the solution for activity measurements. Activity measurements were made with a well-type counter and with a scaler (Type NK-108 from Gamma, Hungary).

From the specific activity (cpm/cm³) of the solutions, the amount of arsenic bound to the resin was calculated by the equation

$$\frac{A}{A_0} = \frac{C_{As}}{C_{oAs}}$$

where A_0 is the initial specific activity of the solution, A is the specific activity of the solution at equilibrium, and C_0 and C are concentrations.

With a knowledge of the amounts of the resins (g) used in the experiments (namely 3.0 ± 0.002 g), their capacities (mequiv./g), the specific activities of the solutions (A_0 and A) and the initial concentration, the apparent equilibrium constant (K^*) and the distribution coefficients (D) could be calculated. The results of the equilibrium experiments are given in Table I.

The chromatographic experiments were carried out on ion-exchange columns of 80 or 165 cm height and 2 or 3 cm diameter. The solution was fed in at the top of the column (input), and had a volume velocity of 10 cm³/min or a linear velocity of 1.41 cm/min. The activity and pH of the effluent (output) were checked continuously during the sorption and elution. The results of these experiments are given in Table II and Fig. 1.

TABLE I

APPARENT ION-EXCHANGE EQUILIBRIUM CONSTANTS (K^*) AND DISTRIBUTION COEFFICIENTS (D) OF ARSENIC(III) ON VARION ANION-EXCHANGE RESINS

pH	Ionic form	K^*			D		
		VARION AD	VARION AT-4	VARION AT-6	VARION AD	VARION AT-4	VARION AT-6
4.6	Cl ⁻	27.1	8.6	13.1	0.98	0.77	0.77
	SO ₄ ²⁻	31.5	20.5	106.7	1.02	1.00	1.21
	HCO ₃ ⁻	127.9	237.8	303.9	1.34	1.72	1.39
	OH ⁻				2.66	3.34	> 1000
7.9	Cl ⁻	43.1	4.1	8.8	1.09	0.6	0.70
	SO ₄ ²⁻	43.1	32.4	44.3	1.09	1.13	1.02
	HCO ₃ ⁻	104.0	469.3	182.2	1.30	1.93	1.30
	OH ⁻				2.16	3.34	1.86

TABLE II

pH AND BREAKTHROUGH CAPACITY IN REMOVAL OF ARSENIC WITH VARION AT-6 RESIN

$-\log K_w = 14.1969$; temperature = 20° (ref. 4). Chromatographic conditions: column length = 1.65 m; diameter = 0.03 m; flow velocity = $10 \text{ cm}^3/\text{min}$; linear velocity = $1.41 \text{ cm}/\text{min}$.

Expt. No.	Input		Output		n ($C_{\text{OH}^-}/C_{\text{As}}$)	Breakthrough capacity (g $\text{As}_2\text{O}_3 \pm 0.5$)
	$C_{\text{As}_2\text{O}_3}$ (g/l)	C_{As} (g-atom/l)	pH (± 0.05)	C_{OH^-} (g-equiv./l)		
1	0.4	$4.04 \cdot 10^{-3}$	11.8	$4.30 \cdot 10^{-3}$	1.064	24
2	0.8	$8.08 \cdot 10^{-3}$	12.1	$8.57 \cdot 10^{-3}$	1.061	24
3	1.0	$10.10 \cdot 10^{-3}$	12.2	$1.08 \cdot 10^{-2}$	1.069	26
4	4.0	$4.04 \cdot 10^{-2}$	12.7	$3.40 \cdot 10^{-2}$	0.817	30
5	40.0	$4.04 \cdot 10^{-1}$	13.7	$3.40 \cdot 10^{-1}$	0.842	10

RESULTS AND DISCUSSION

It can be seen from the distribution coefficients and equilibrium constants shown in Table I that the sorption affinity of the VARION AD resins for arsenic is weaker than that of the VARION AT resins. It has been established¹ that their sorption affinity is similar to that of silicate ions. All three resins in the OH^- form show the highest affinity for arsenic ions.

According to the equilibrium data, chromatographic experiments were planned on both laboratory and pilot-plant scales.

During these "dynamic" measurements, the effect of the "input" arsenic content was studied in terms of the pH of the effluent (output) and the breakthrough capacity. Some of the results are summarized in Table II and Fig. 1. The results show that in the steady-state sorption of arsenic from "input solution" the arsenic concen-

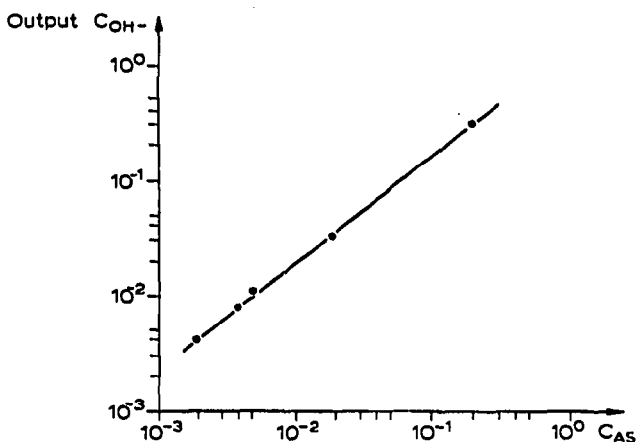


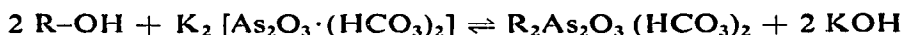
Fig. 1. OH^- concentration (C_{OH^-}) of the effluent versus arsenic content of the solutions fed into the VARION AT-6 ion-exchange column. Column height, 1.65 m; diameter, 0.03 m; volume of resin, 1.166 l.

tration determines the pH value in the "output". The ratio n of C_{OH^-} ,_{output} to the arsenic concentration of the solution fed into the ion-exchange column, C_{As} ,_{input}, is almost unity (Table II, 6th column), *i.e.*, each equivalent of arsenic corresponds to one equivalent of hydroxide. Fig. 1 shows that there is a linear relationship between $\log C_{\text{OH}^-}$ and $\log C_{\text{As}}$. The slope of the graph can be evaluated according to the equation

$$\frac{\Delta \log (C_{\text{OH}^-}, \text{output})}{\Delta \log (C_{\text{As}}, \text{input})} = 1.001$$

which shows that one equivalent of hydroxide corresponds to one equivalent of arsenic in the sorption of arsenic on the anion-exchange resins in the OH^- form.

These results are in agreement with those of other workers. According to Stehlík², in strongly alkaline solution the metaarsenite form exists, and according to Ephraim³ it is able to form complex arsenic-carbonate compounds with the carbonate in the solution. In more strongly alkaline and concentrated solutions, the association of arsenic to produce diarsenite ions can be the cause of a decrease in n (Table II, experiments 4 and 5). Taking in consideration the above, the following equation could perhaps be assumed for an overall equilibrium:



where R is the resin matrix (cross-linked polystyrene).

Other experiments were carried out to study the effect of arsenic concentration on the breakthrough capacity of the ion-exchange column. The results given in the last column in Table II show that an increase in the arsenic concentration causes a decrease in the breakthrough capacity of the column.

When the column was loaded with a solution containing 40 g/l of arsenic(III) oxide, the pH of the effluent increased to 13.7. In this case the liberated OH^- ions prevent the necessary sorption of arsenic ions. According to the second column of Table II, working with an input concentration of arsenic(III) oxide of 4 g/l, the pH of the output is 12.7. The arsenic concentration in this effluent is 4 mg/l as arsenic(III) oxide, which is satisfactory for our purposes.

According to these experiments, a method has thus been developed for removing arsenic from alkaline waste water, by which the concentration of the arsenic can be reduced to less than 4 mg/l as arsenic(III) oxide⁵.

The elution of the sorbed arsenic from the resin was carried out with 1 M potassium hydroxide solution. By this means, the arsenic can be eluted with a sharp peak. After elution of the arsenic, the resin is in the OH^- form again and can be loaded repeatedly with arsenic.

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