

The position of halide anions and their sequence of adsorption on aluminium oxide

The sequence of adsorption for halide anions on alumina was first established by KUBLI in 1947¹. In that work he completed the anion sequence presented earlier by SCHWAB². In addition to KUBLI, GAPON AND SHUVAJEVA³ and OLSHANOVA AND CHMUTOV⁴ studied the same subject independently. According to all of these authors, the sequence was found to be as follows: $I^- > Br^- > Cl^-$. On the other hand, the sequence of halide anions on paper impregnated with aluminium hydroxide has, according to FLOOD⁵, the following order: $I^- < Br^- < Cl^-$. The author of this paper established the same order as FLOOD for halide anions on three ferric hydroxides⁶ and on hydrous zirconium oxide⁷

It seemed to be useful to find out the reasons why the behaviour of alumina on the one hand, and ferric and zirconium hydroxides on the other, are different.

Preliminary studies, carried out by the author of this paper on alumina produced by POCh Gliwice, provided results that were contradictory to those obtained by KUBLI and the Russian investigators mentioned. Therefore, it was decided to repeat the experiments employing alumina from various sources, in order to exclude the possible effect of the sorbent preparation on the sequence of halide anions.

Experimental

Sorbents

Aluminium oxide for chromatography, POCh Gliwice, Poland.

Aluminium oxide for chromatography, Fluka, type 507 c.

Aluminium oxide, pure, U.S.S.R.

Aluminium Oxide G for thin layer chromatography, Merck.

Aluminium oxide loaded paper – Schleicher and Schüll.

Methods

Column chromatography. Alumina was washed with 0.2 M KNO_3 on a sintered glass funnel until no test for chloride was obtained. Subsequently, the sorbent was treated with 0.2 M HNO_3 in order to convert the alumina into the "acid" form. Glass tubes 3.2 mm internal diameter were packed with sorbent suspended in 0.2 M HNO_3 . Columns 10–30 cm long were used. 0.1 M potassium halide salt solutions in 0.2 M KNO_3 were prepared and mixed in equal volumes. 0.05 ml samples were added to the top of the column and the anions were eluted with 0.2 M KNO_3 at a flow rate of 20–70 cm/h.

The effluent was analysed by the following methods: spot analysis⁸, a radio-metric method and a chromato-polarographic method⁹ modified for anion analysis by the author of this paper¹⁰.

Thin-layer chromatography. 25 g of Aluminium Oxide G were suspended in 50 ml of 0.2 M HNO_3 . The glass plates (20 × 20 cm) were coated with this suspension to a thickness of 0.5 mm. μ l amounts of the anions in the form of 0.1 M solutions of their potassium salts were applied on the plates which were developed with 0.2 M KNO_3 . The length of the run was 16 cm.

Preparation of the aluminium oxide loaded paper. The aluminium oxide loaded paper, Schleicher and Schüll, was washed by a descending technique in the chromato-

graphic chamber with 0.2 M KNO_3 , till all the Cl^- ions were eluted and next with 0.2 M HNO_3 . After drying, $2\mu\text{l}$ of an 0.1 M solution of the anions were placed on the paper, and the chromatograms were developed by the ascending technique with 0.2 M KNO_3 . The length of the run was 20 cm. Both the thin-layer and paper chromatograms were visualized with an ammoniacal solution of AgNO_3 and fluorescein¹¹.

A radioautographic technique was also employed and the following radioactive isotopes were used: $^{131}\text{I}^-$, $^{82}\text{Br}^-$, $^{36}\text{Cl}^-$. Radioautographs were prepared by placing the dried chromatogram on an X-ray film, which after a definite time of exposure was developed and fixed in a usual way.

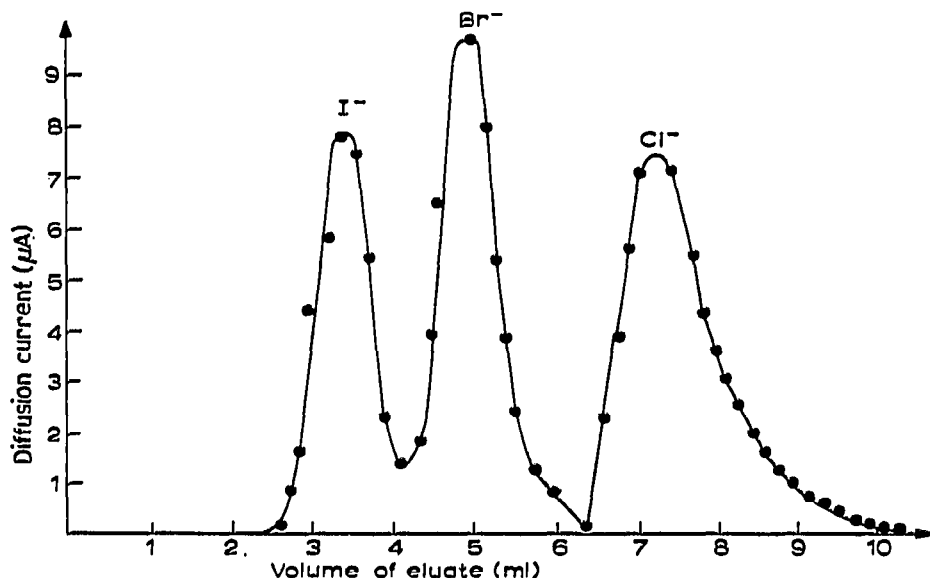


Fig. 1. Separation of I^- , Br^- and Cl^- on aluminium oxide. Column $0.075\text{ cm}^2 \times 29.5\text{ cm}$. Flow rate 31 cm/h.

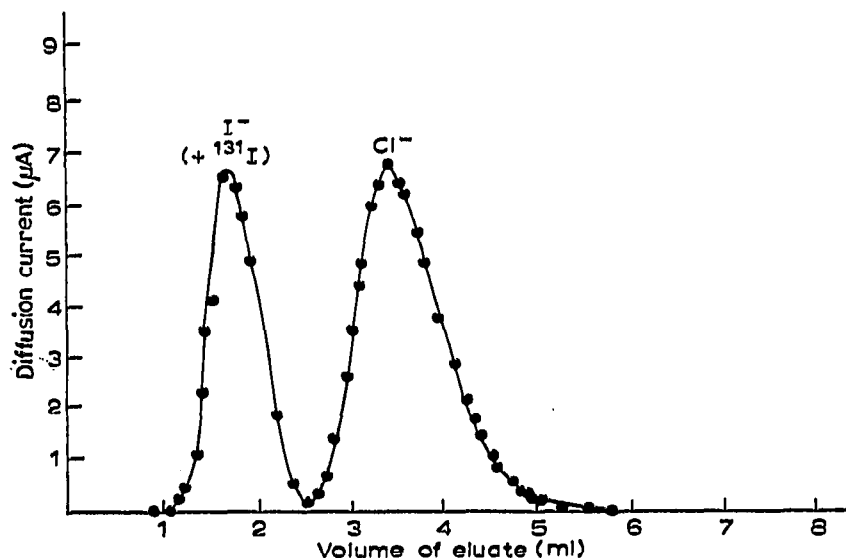


Fig. 2. Separation of I^- and Cl^- on aluminium oxide. Column $0.075\text{ cm}^2 \times 11\text{ cm}$. Flow rate 27 cm/h.

Results

Regardless of the technique employed the sequence of adsorption for the halide anions on aluminium oxide was as follows: $I^- < Br^- < Cl^-$. The elution curve of the Cl^- , Br^- , I^- mixture from the $0.075 \text{ cm}^2 \times 29.5 \text{ cm}$ alumina column, plotted by the chromatopolarographic method is shown in Fig. 1. Although the column used was very long, no complete separation of anions was obtained. Complete separation of a mixture of only I^- and Cl^- was obtained on a column, the dimensions of which were $0.075 \text{ cm}^2 \times 11 \text{ cm}$ (Fig.2). In this experiment the analysed solution contained $^{131}I^-$. After leaving the polarographic cell the effluent was collected in the form of single drops by means of a fraction collector. The activity of the drops was determined with a well-type scintillation counter. The activity curve coincided exactly with the elution curve obtained by the polarographic method.

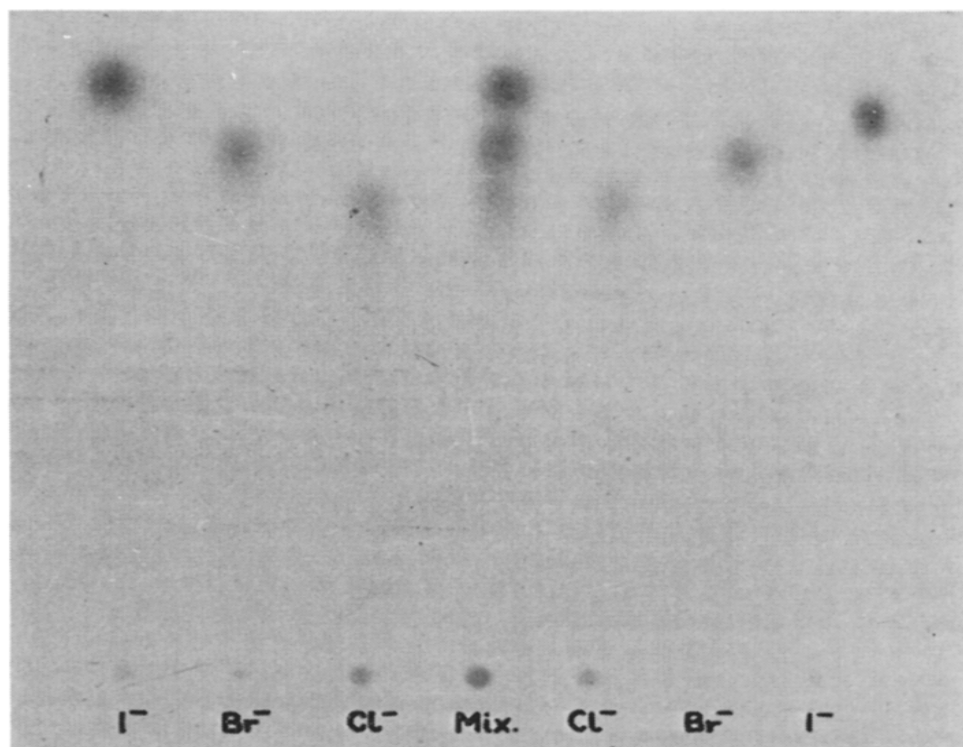


Fig. 3. Chromatogram of halide anions (radioautograph). Conditions: Chromatoplate ($20 \times 20 \text{ cm}$) made of acidified Aluminium Oxide G. Developed with 0.2 M KNO_3 . Length of run 16 cm .

Fig. 3 presents the radioautograph of the chromatogram of the labeled halides mixture on the Aluminium Oxide G layer. Similar results were obtained on the aluminium oxide loaded paper, but the separation was not as good.

Discussion

It is evident from the results that the order of the adsorption sequence for halide anions was as follows: $Cl^- > Br^- > I^-$. In all the alumina preparations studied the order was identical, and did not depend on the separation techniques used. In the case of the column technique, the order in which anions were eluted established their sequence of adsorption. With regard to KUBLI's results¹ the discrepancy is likely to be caused by the technique he used to visualize the bands of separated anions directly

on the column. This technique consists of passing the visualising solution through the column, which initiates an additional chromatographic process. It is possible that in some cases this procedure leads to erroneous results.

A similar order for the halide anions on alumina, ferric hydroxides⁶ and zirconium hydroxide⁷ points to the existence of a common mechanism of anion sorption on inorganic sorbents of the hydroxide type. It seems that the factor which may be decisive in the sorption of anions is their affinity towards the hydroxide-forming metal. This affinity depends on the solubility of the corresponding salts (sorbing anion and hydroxide-forming metal), instability of complexes, and the tendency towards hydrolysis of the bonds that are formed during the sorption process.

Ionic sieve properties, which play the main role in the processes occurring in organic resins, as well as in the case of cation sorption on inorganic ion exchangers, need not be taken into consideration here. The behaviour of the fluoride ion may render an explicit example. The sorption of this anion on alumina², and on ferric hydroxides⁶ is strong, but in the case of Dowex 2¹² for instance, its sorption is the weakest of all halides due to a low ionic radius.

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