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## THIN-LAYER CHROMATOGRAPHY OF INORGANIC ANIONS ON ALUMINIUM OXIDE\*

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### SUMMARY

The adsorption of inorganic anions on alumina thin layers developed with aqueous salts, acids and bases was studied. The effect of pH and salt concentration is discussed and the adsorption compared with the tendency for the formation of ion pairs between anions and  $Al^{3+}$  as observed in paper electrophoresis.

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### INTRODUCTION

The first separations of inorganic ions were carried out on alumina columns in 1937<sup>1,2</sup> and since then numerous mechanisms of the adsorption process have been proposed both for cations and anions. Most of these mechanisms deal mainly with cations and have been reviewed and discussed by Sacconi<sup>3</sup> and Hayek<sup>4</sup>. Work on anions was done mainly by displacement analysis on both columns<sup>1,2,5,6</sup> and loaded filter-papers, yielding an elution sequence that was more or less the same in all investigations.

Interest in alumina was revived when inorganic ion exchangers were studied more extensively. Aluminium oxide, being classed as a hydrous oxide (like zirconium and titanium oxides), was shown to adsorb anions by a law of mass action equilibrium. However, the only equilibrium studied in this connection was the  $Br^- - NO_3^-$  system on  $ZrO_2$ <sup>7</sup>.

Another interesting aspect of the adsorption of anions was obtained by Hayek and Schimann<sup>8</sup>, who compared the adsorption sequence of anions on  $Al_2O_3$ ,  $La_2O_3$ ,  $Bi_2O_3$ ,  $ZnO$  and  $PbO$  and obtained different sequences that were in the order of the solubilities of the respective salts formed between the metal of the oxide and the anion.

A study of the adsorption of U(VI) and several other cations and anions on papers impregnated with various metal oxides<sup>9</sup> showed that cations such as Ni, Co, Cu and Fe(III) were desorbed from  $TiO_2$  and  $ZrO_2$  with increasing LiCl concentration. No such "law of mass action" desorption could be observed with chromate; the  $R_F$  values were reasonably constant over wide ranges of LiCl concentrations (1-10 N).

The present work deals with the thin-layer chromatography of inorganic anions on aluminium oxide thin layers. Preliminary results had shown that on these layers

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\* Dedicated to Professor Edgar Lederer on his 65th birthday.

excellent chromatograms with sharp separations could be obtained with aqueous solutions as the eluent. Separations of halo-acids with organic solvents had been described previously using mixed silica gel-aluminium oxide layers<sup>10</sup> and I<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup> (in that order) were separated by Tustanowski<sup>11</sup> on acidified Al<sub>2</sub>O<sub>3</sub> thin layers, developing with 0.2 *N* KNO<sub>3</sub>.

## EXPERIMENTAL

All chromatography was carried out with MN-Polygram Alox N aluminium oxide thin layers on plastic sheets (Macherey-Nagel Co., Düren, G.F.R.) in 4.5 × 10 × 14.5 cm glass jars covered with glass lids. The aqueous solvents were poured into each jar to a height of *ca.* 5 mm and the 4 × 13 cm thin layers stood in the solvent. After development, which took 30 min, the thin layers were placed on blotting paper and sprayed lightly with suitable reagents.

## RESULTS AND DISCUSSION

We commenced this study in order to examine the behaviour of the perbromate ion on alumina. We ran several related but less valuable anions in preliminary studies, so that most of the results were obtained with a mixture of IO<sub>4</sub><sup>-</sup>-IO<sub>3</sub><sup>-</sup>-BrO<sub>3</sub><sup>-</sup> and a spot of CrO<sub>4</sub><sup>2-</sup> run next to it. In these experiments, the chromatograms were sprayed lightly with KI in 1 *N* HCl for detection.

### *Neutral solutions of monovalent anions as eluents*

Table I shows the *R<sub>F</sub>* values obtained with various monovalent anions as eluents.

It is evident that there is no appreciable change in *R<sub>F</sub>* value for the various anions as the concentration of the eluent anion increases from 0.1 to 1 *N*, nor any *R<sub>F</sub>* difference between the anions used as eluents. This result is in striking contrast to the results observed on anion-exchange resins, *e.g.*, on SB-2 strong anion-exchange resin paper, as shown in Fig. 1.

Clearly, there is a "law of mass action" type of adsorption on the SB-2 paper that does not occur on alumina. Increasing the electrolyte concentration still higher has limitations, as the thin layers are not wetted by LiCl at concentrations above 2.5 *N*. However, even with 2.5 *N* LiCl, the *R<sub>F</sub>* values for all of the anions are essentially those found at lower concentrations.

Fig. 2a shows the *R<sub>F</sub>* values of a large number of anions developed with 1 *N* KCl. All monovalent anions except iodate and periodate are only slightly adsorbed and have high *R<sub>F</sub>* values, while all divalent and polyvalent anions, with the exception of hexacyanoferrate(III), are strongly adsorbed. At this stage, it is interesting to compare these results with the *R<sub>F</sub>* values obtained on a resin anion-exchange paper (Fig. 2b) and a sequence of anions obtained by displacement development<sup>6</sup> (Fig. 2c).

Comparing alumina with the anion-exchange resin, it can be seen that alumina does not possess the pronounced affinity differences for halides, and also that the resin does not adsorb all polyvalent anions strongly, while alumina does. The sequence is thus entirely different from that on the resin. If we compare the *R<sub>F</sub>* values obtained

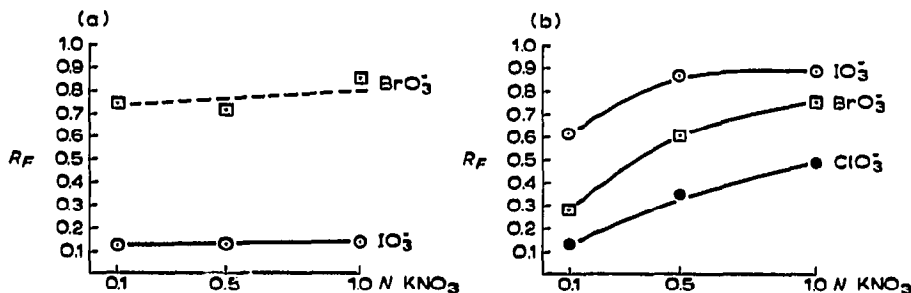
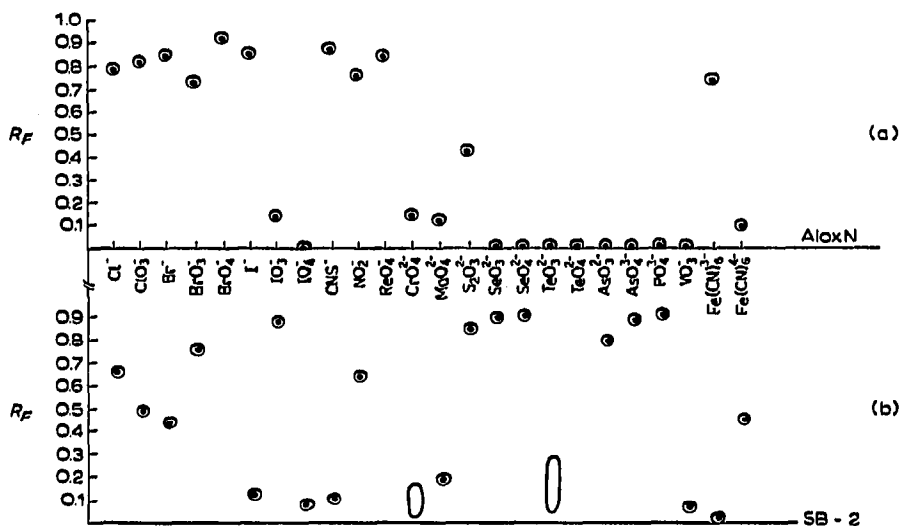


Fig. 1.  $R_F$  values plotted against the concentration of  $KNO_3$  used as eluent: (a) for alumina thin layers; (b) for SB-2 anion-exchange resin paper.



	OH <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , F <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup> , Fe(CN) <sub>6</sub> <sup>4-</sup> , CrO <sub>4</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup>	Fe(CN) <sub>6</sub> <sup>3-</sup> , Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup> , CNS <sup>-</sup>	I <sup>-</sup> , Br <sup>-</sup> , Cl <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , MnO <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , S <sup>2-</sup>
$R_F$ values for comparison	0	Fe(CN) <sub>6</sub> <sup>4-</sup> = 0.09, 0.41 CrO <sub>4</sub> <sup>2-</sup> = 0.14		Fe(CN) <sub>6</sub> <sup>3-</sup> = 0.73	CNS <sup>-</sup> = 0.87	0.85, 0.84, 0.78, 0.75, fast, but decomposes

Fig. 2. Schematic representation of  $R_F$  values of inorganic anions: (a) on alumina thin layers (developed with 1 N  $KNO_3$ ); (b) on SB-2 anion-exchange resin paper (developed with 1 N  $KNO_3$ ); (c) displacement sequence (according to Kubli<sup>6</sup> of inorganic anions on alumina with  $R_F$  values from (a) below each anion.



here with the displacement elution sequence, it can be seen that a relatively good agreement exists if one takes into account the differences in procedure.

### *pH effects*

The  $R_F$  values in various acids and bases and in acetate buffers are given in Table II.

In ammonia and sodium carbonate, there is a very strong desorption of the anions, except for periodate, which remains at  $R_F = 0$ .

Acetate buffers do not show any change in  $R_F$  value above pH 5. At pH 4.3, the iodate spot has a pronounced tail and at pH 3.7 it remains at the point of application.

Fig. 3 shows the  $R_F$  values of a range of anions in 1 *N*  $\text{Na}_2\text{CO}_3$ . There is a general tendency for higher  $R_F$  values to occur in 1 *N*  $\text{Na}_2\text{CO}_3$  than in 1 *N*  $\text{KNO}_3$ , especially for those anions with  $R_F$  values in the region of 0.2 in 1 *N*  $\text{KNO}_3$ . However, some anions, such as tellurite, tellurate and periodate, remain at the point of application, even in 0.1 *N*  $\text{Na}_2\text{CO}_3$ .

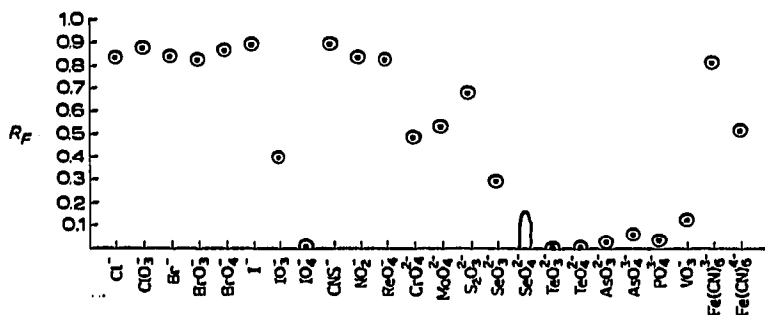


Fig. 3. Schematic representation of  $R_F$  values of inorganic anions on alumina thin layers developed with 0.1 *N*  $\text{Na}_2\text{CO}_3$ .

The pH effects agree fairly well with the surface equilibria previously suggested<sup>12</sup>:



In HCl, the results differ with the acidity of the solution chromatographed. If iodate is dissolved in HCl, it remains at  $R_F = 0$  in 0.5 and 1 *N* HCl but not in 0.1 *N* HCl. Chromate applied as a neutral aqueous solution is not adsorbed more strongly than when water is the eluent. When dissolved in 0.1 *N* HCl and applied as such, it is at  $R_F = 0$  in 0.1 and 0.5 *N* HCl but has the same  $R_F$  value as chromate in 1.0 *N* HCl. These results illustrate the limitations of all  $R_F$  values quoted here, which are valid only, when neutral aqueous solutions are chromatographed.

### *Eluents containing complexing and polyvalent anions*

Much higher  $R_F$  values are obtained with sulphate, phosphate and fluoride as eluents than with nitrate, chloride and perchlorate, as shown in Table III. Not only are the  $R_F$  values higher, but they increase with an increase in the eluent concentration.

TABLE III

$R_F$  VALUES OF SOME INORGANIC ANIONS ON MN-POLYGRAM ALOX N THIN LAYERS DEVELOPED WITH SULPHATE, PHOSPHATE AND FLUORIDE

Ion	Eluent									
	$K_2SO_4$			$K_3PO_4$				$NaF$		
	0.1 N	0.5 N	1.0 N	0.05 N	0.1 N	0.5 N	1.0 N	0.1 N	0.5 N	1.0 N
$IO_3^-$	0.27	0.33	0.40	0.33	0.39	0.52	0.64	0.29	0.41	0.47
$BrO_3^-$	0.78	0.83	0.83	0.84	0.81	0.76	0.81	0.79	0.80	0.80
$CrO_4^{2-}$	0.43	0.55	0.57	0.47	0.50	0.56	0.72	0.48	0.49	0.51
$IO_4^-$	0	0	0	0	0	0	0	0	0	0

The cationic aluminium on the surface enters into competition with the more strongly held eluent anion and thus displaces the anions to be separated. The mechanism may be different in each case: with fluoride, by complexation; with sulphate, more likely by outer-sphere complexing; and with phosphate, by both of these mechanisms as well as by a pH effect due to the hydrolysis of the triphosphate ion.

#### Some separations of mixtures

Some mixtures of anions were separated in 0.1 N  $Na_2CO_3$  and are shown in Fig. 4. The presence of another anion influences the movement of a particular anion, especially when they are moving near each other and thus are subject to displacement effects. The mixture  $MoO_4^{2-}-VO_3^- - ReO_4^-$  separates with  $R_F$  values close to those of the pure substances, but even with such large  $R_F$  differences some changes occur.

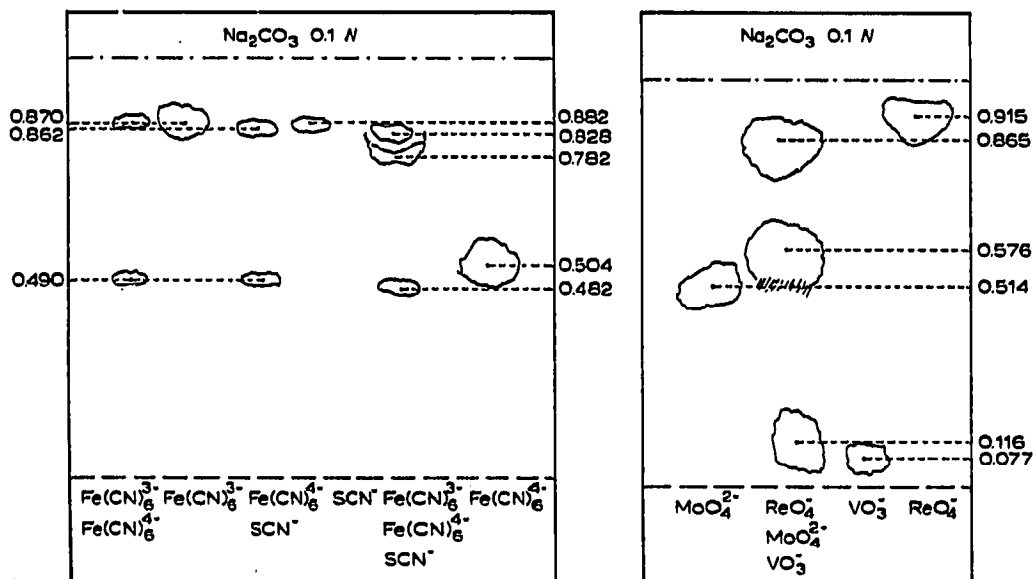


Fig. 4. Some separations of anions with aqueous 0.1 N  $Na_2CO_3$  as eluent. (a) Mixtures of hexacyanoferrate(II), hexacyanoferrate(III) and thiocyanate and pure substances run side by side. Note the "displacement" effect in the ternary mixture. (b) Mixtures of perrhenate, molybdate and vanadate and the pure substances run side by side.

### Some considerations of the possible mechanisms involved

There seems to be evidence<sup>7</sup>, although only for a few examples such as the  $\text{Br}^- - \text{NO}_3^-$  equilibrium, that an adsorption obeying the law of mass action exists on alumina. Our results seem to indicate, however, that in addition to this type of adsorption there are also other types that do not obey the law of mass action.

The observation by Hayek and Schimann<sup>8</sup> that the sequences obtained are related to the solubilities of the respective salts could help to explain the results obtained here, but it is limited to exact pH conditions (as already pointed out by Hayek and Schimann<sup>8</sup>). Furthermore, good zones should form only with very dilute solutions of the anion to be chromatographed, and under such conditions it is not possible to obtain an excess of anion compared with the amount of  $\text{Al}^{3+}$  available but rather an excess of ionized aluminium for a given anion. Under such conditions, precipitates do not form, but soluble ion pairs and/or complexes form readily and can be detected by electromigration experiments on paper<sup>13</sup>.

There is a rather good correlation for most anions if one compares electromigration in 0.5 *N* aluminium nitrate with adsorption on alumina from neutral solutions, as shown schematically in Fig. 5.

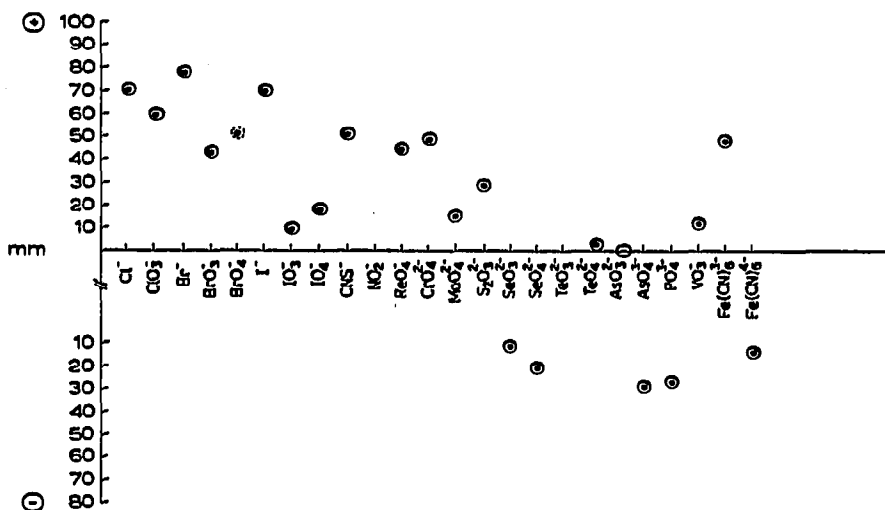


Fig. 5. High-voltage paper electrophoresis of inorganic ions in 0.5 *N*  $\text{Al}(\text{NO}_3)_3$ . Whatman No. 1 paper; Camag high-voltage apparatus. Voltage, 1000 V for 30 min. Some of the data are taken from Ref. 13 and the remainder were obtained in this study. The value for perbromate (dotted line) is that for 0.1 *N*  $\text{Al}(\text{NO}_3)_3$  obtained earlier<sup>14</sup>; it serves only to point out that perbromate moves rather quickly.

Actually, all anions that move quickly in electrophoresis have high  $R_F$  values on alumina thin layers and all those which are cationic or near the point of application are strongly adsorbed, with the exception of  $\text{CrO}_4^{2-}$ , which moves rather quickly in electrophoresis and is strongly adsorbed on alumina. This correlation, however, states only that an anion that experiences a retardation in electromigration when moving in a solution of aluminium nitrate also adsorbs on alumina layers. It does not explain why there is no "law of mass action" type of desorption from alumina when

eluted with monovalent electrolytes. Electromigration in mixtures of  $\text{Al}^{3+}$  and  $\text{NH}_4^+$  would suggest that the interaction between the anions and  $\text{Al}^{3+}$  should be reversible<sup>14</sup>. Also, the fact that most anions are desorbed by  $\text{Na}_2\text{CO}_3$ ,  $\text{NaF}$ , etc., would indicate that the "adsorption" is reversible.

We cannot offer an explanation at the moment why the adsorption does not follow the law of mass action. However, this behaviour seems to be one of the important properties of alumina and seems to merit more attention.

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