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Note

The adsorption of inorganic anions on hydrous oxides

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In a study of the thin-layer chromatography of inorganic anions on alumina, we had noted a strong similarity with the adsorption sequence obtained with the electrophoretic sequence of the same ions when subjected to electrophoresis on paper in aluminium nitrate as electrolyte¹. This strongly suggested a similarity between adsorption and ion-pair formation.

A completely different similarity has been observed by Hayek and Schimann² between the adsorption sequence (by displacement analysis) and the solubility of the respective salts between the cation of the hydrous oxide and the anions chromatographed. Furthermore, two different sequences were noted on alumina and silica gel for a series of cobalt complexes³.

We therefore felt that it would be interesting to compare various hydrous oxides as supports for the chromatography of inorganic anions, and our findings are reported in this paper.

The exact nature of the surface of hydrous oxides depends on the method of precipitation and the age of the precipitate. In order to obtain products with reasonable activity, the simplest method was to precipitate the hydrous oxides inside filter papers and to compare the behaviour of the various impregnated filter papers. The only exception was silica gel, for which we employed silica gel G₂₅₄ TLC plates (Merck, Darmstadt, G.F.R.).

EXPERIMENTAL

Preparation of filter papers impregnated with hydrous oxides

Whatman No. 1 paper strips were impregnated with 1 *M* solutions of salts of the respective metals and hung in chromatography jars that contained concentrated ammonia solution at the bottom, *i.e.*, in a saturated ammonia atmosphere, for 1 day to precipitate the hydroxide. The strips were then washed three times with distilled water, allowing 30 min contact for each wash, and allowed to dry overnight at room temperature between sheets of blotting paper.

Chromatography

All chromatograms were developed by the ascending method in wide-mouthed glass jars closed with rubber stoppers. The solvent was always 1 *N* potassium nitrate

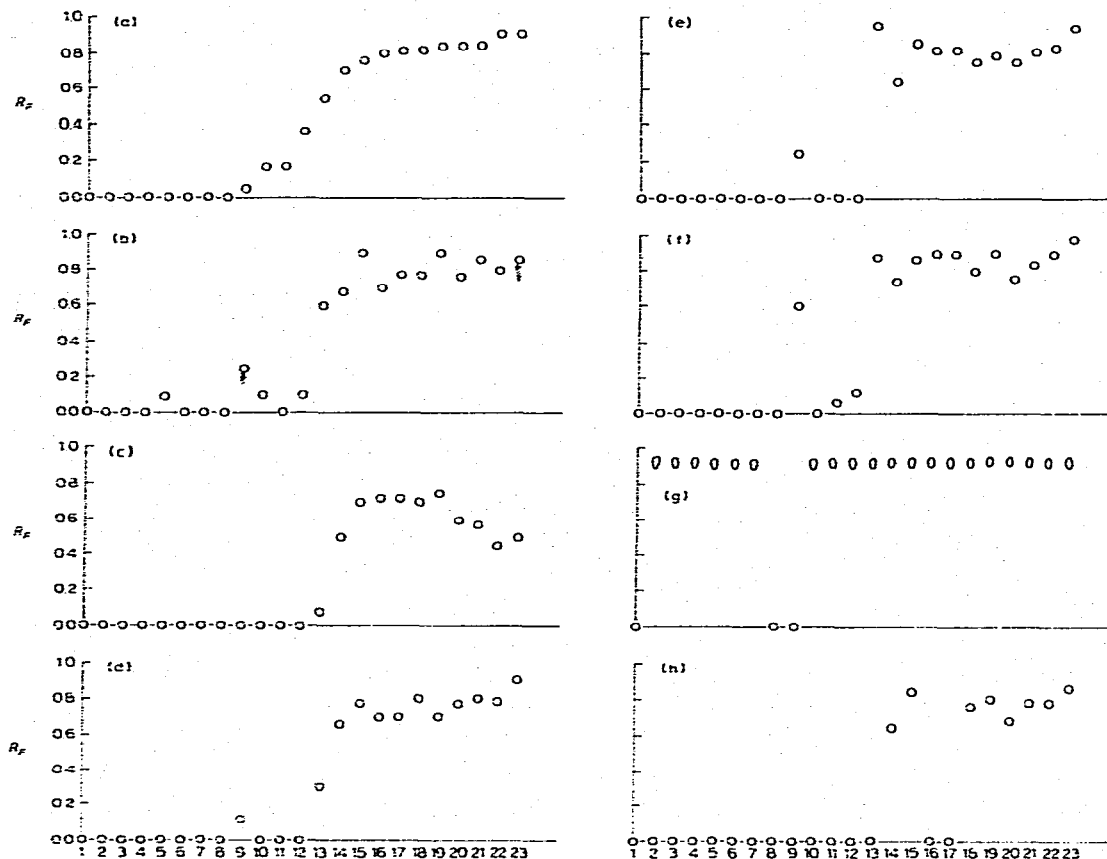


Fig 1. Graphical representation of the R_F values of anions on papers impregnated with various hydrous oxides. (a), $\text{Al}(\text{OH})_3$; (b), $\text{La}(\text{OH})_3$; (c), ThO_2 ; (d), ZrO_2 ; (e), TiO_2 ; (f), SnO_2 ; (g), SiO_2 (silica gel F_{254} thin-layer plate); (h), $\text{Bi}(\text{OH})_3$. Anions: 1 = VO_3^- ; 2 = IO_3^- ; 3 = PO_4^{3-} ; 4 = AsO_4^{3-} ; 5 = AsO_2^- ; 6 = SeO_3^{2-} ; 7 = TeO_4^{2-} ; 8 = TeO_3^{2-} ; 9 = $\text{Fe}(\text{CN})_6^{4-}$; 10 = MoO_4^{2-} ; 11 = CrO_4^{2-} ; 12 = IO_3^- ; 13 = $\text{S}_2\text{O}_3^{2-}$; 14 = ReO_4^- ; 15 = ClO_3^- ; 16 = I^- ; 17 = Br^- ; 18 = BrO_3^- ; 19 = Cl^- ; 20 = CNS^- ; 21 = NO_2^- ; 22 = BrO_3^- ; 23 = $\text{Fe}(\text{CN})_6^{3-}$.

solution and the front was allowed to move *ca.* 15 cm. The paper was then sprayed with the usual spot test reagents to reveal the positions of the anions.

RESULTS AND DISCUSSION

The results are shown graphically in Fig. 1. It can be seen that there is a group of anions that are strongly adsorbed on virtually all supports, then a group with intermediate R_F values: hexacyanoferrate(II), molybdate, chromate, iodate and thio-sulphate, which have different R_F values on different hydrous oxides. For the tetravalent hydrous oxides, the R_F values increase in the order $\text{ThO}_2 < \text{ZrO}_2 < \text{TiO}_2 < \text{SnO}_2$, which is also the order of decreasing basicity⁴. Finally, there is a large group of anions that travel near the liquid front but have lower R_F values on the more basic exchangers such as ThO_2 and $\text{La}(\text{OH})_3$.

Two hydrous oxides need further comment: on bismuth oxide, the overall picture is the same, but iodide, bromide, thiosulphate and iodate are also at $R_F = 0$. We suggest that in addition to the usual mechanism, complex formation also takes place, at least in the case of iodide and bromide.

On silica gel, all ions travel with the liquid front except for tellurite, vanadate and hexacyanoferrate(II). As we developed the chromatograms with neutral potassium nitrate solution on the rather acidic silica gel, it seems probable that TeO_2 was precipitated or TeO^{2+} was adsorbed and that vanadate was adsorbed as the vanadyl cation. Hexacyanoferrate(II) was probably precipitated as its zinc salt as a result of the presence of trace amounts of zinc ions in the thin-layer plate.

Apart from the above exceptions, it is interesting that the overall picture is essentially the same on all hydrous oxides (except, of course, on silica gel) and that this is also the order of electrophoretic movement in aluminium nitrate and thus the order of ion-pair formation.

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