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Note

The thin-layer gel chromatography of polymeric hydrolysis products of metal ions

Numerous metal ions yield soluble polymers as intermediates in the precipitation of insoluble hydroxides. Their study by ion-exchange[1] and by paper partition chromatography[2] permits their detection but does not help in their characterisation.

OHASHI *et al.*[3] have shown that polyphosphates, down to even dimers and trimers, can be separated on highly cross-linked Sephadex columns. Later, HENRY AND ROGERS[4] and KITAYEVITCH *et al.*[5] studied the hydrolysis products of Fe(III) and Ru(IV) nitrosyl by column gel chromatography and in both instances an excluded fraction was observed.

Our interest lay mainly in the type of hydrolysis polymer formed by Zr(IV) even in acidic solutions, which yield comets in most of the usual chromatographic systems. Ultracentrifuge studies of Zr(IV) by JOHNSON AND KRAUS[6] indicated that a polymer with a molecular weight of about 30,000 exists.

Instead of the column method used by HENRY AND ROGERS[4], we wanted to try thin-layer techniques, as they permit the comparison of low- and high-molecular-weight substances on the same plate under identical conditions. As shown in the results discussed below, we also could observe comet formation and precipitation, so that a much better picture of the behaviour of hydrolysed metal ions is obtained even if the results are less quantitative and more comparative.

Experimental

Sephadex G gels, superfine (dry particle diameter 10–40 μ), and Bio-Gel polyacrylamide gels of the P series (dry particle diameter 40 μ) were used.

The gels were allowed to swell in the eluent for 1–3 days (depending on the extent of the cross-linking) and spread on 5 × 11 cm glass slides with a spreader supplied with the apparatus by Pharmacia Fine Chemicals.

The slides were placed in a development chamber with filter-paper wicks (Whatman No. 3MM paper) at an angle of 15–20° and equilibrated overnight, and then 2–3 μl samples were placed on the layer by means of a micropipette.

Dextran Blue 2000 (Pharmacia) was used as a reference substance to indicate the void volume and $Co(NH_3)_6^{3+}$ as a reference substance for the movement of a small molecule (or ion). Development was usually carried out for 1–3 h, depending on the type of gel.

Results

Preliminary work with Bio-Gel P-2 and Sephadex G-25 layers and elution with 0.01 *N* HNO_3 produced spots on or near the point of application with hydrolysed solutions of Fe(III) and Zr(IV). This "adsorption" or precipitation could be due

to the carboxyl groups of the gels which, as shown recently by ORTNER AND PACHER[7], can play an important role in gel filtration.

Much better results (as shown below) were obtained when acetate buffer or trichloroacetate was used as eluent, especially at concentrations at or above 0.5 *N*. These solutions could act either by competing with the carboxyl groups of the gel or by complexing or forming ion pairs with the charges on the polymers. Whichever it is, it causes a rather severe limitation for the general study of hydrolysed species.

We shall now discuss the results obtained with several metal ion solutions.

Fe(III). Fig. 1 shows the behaviour of a solution of $Fe(NO_3)_3$ and the same solution to which various amounts of $NaHCO_3$ were added. The more hydrolysed solution yields two spots on the very strongly cross-linked gels, of which the faster moves with the speed of Dextran Blue, *i.e.*, it is completely excluded. In the gels with larger pores, there is only one spot, with the speed of small ions. The hydrolysed solutions also leave a slight comet, indicating some precipitation.

Hence it can be concluded that the polymeric hydrolysis product formed coexists with monomeric or small polymeric species that cannot be distinguished from the monomer on the gels.

Zr(IV). The results are shown in Fig. 2. All solutions of Zr(IV) are excluded from the strongly cross-linked gels, moving with the speed of Dextran Blue. On the gels with larger pores they still move faster than monomeric ions.

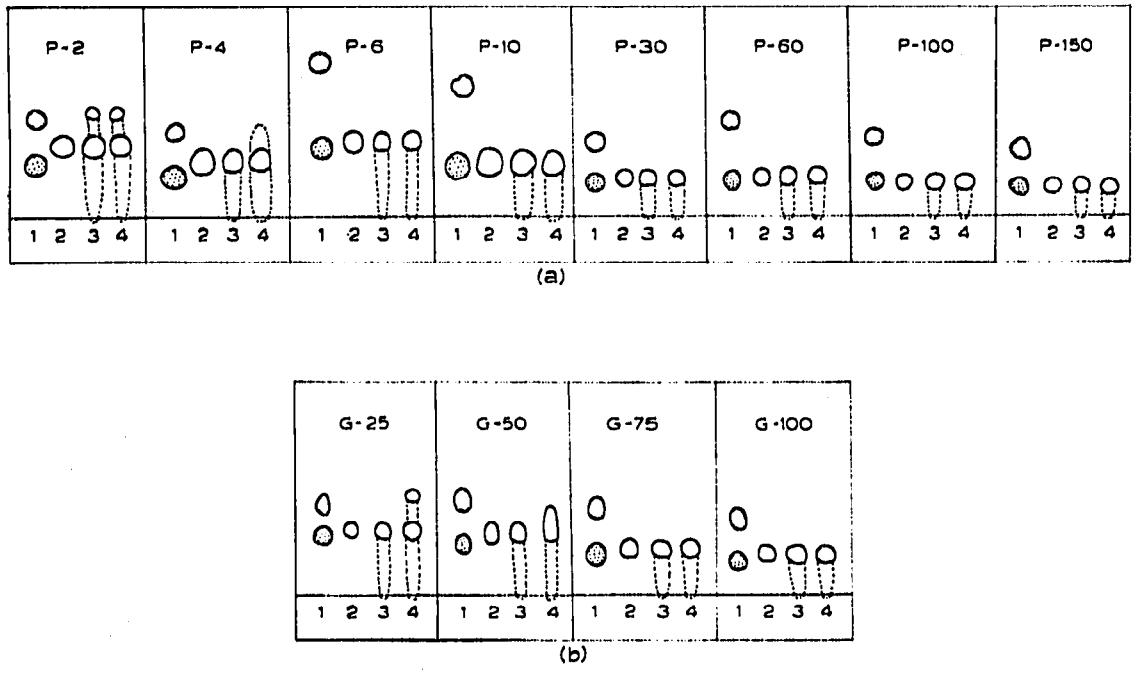

Fig. 1. Chromatograms obtained with 0.5 *N* acetate buffer as eluent on thin layers of (a) Bio-Gel polyacrylamide gels and (b) Sephadex G gels. Samples applied: (1) Dextran Blue 2000 and $Co(NH_3)_6^{3+}$ as reference substances; (2) fresh 0.1 *M* solution of $Fe(NO_3)_3$; (3) solution with OH–Fe ratio = 1, (*i.e.* 1 mole of $NaHCO_3$ added to 1 mole of Fe^{3+}); (4) solution with OH–Fe ratio = 2.

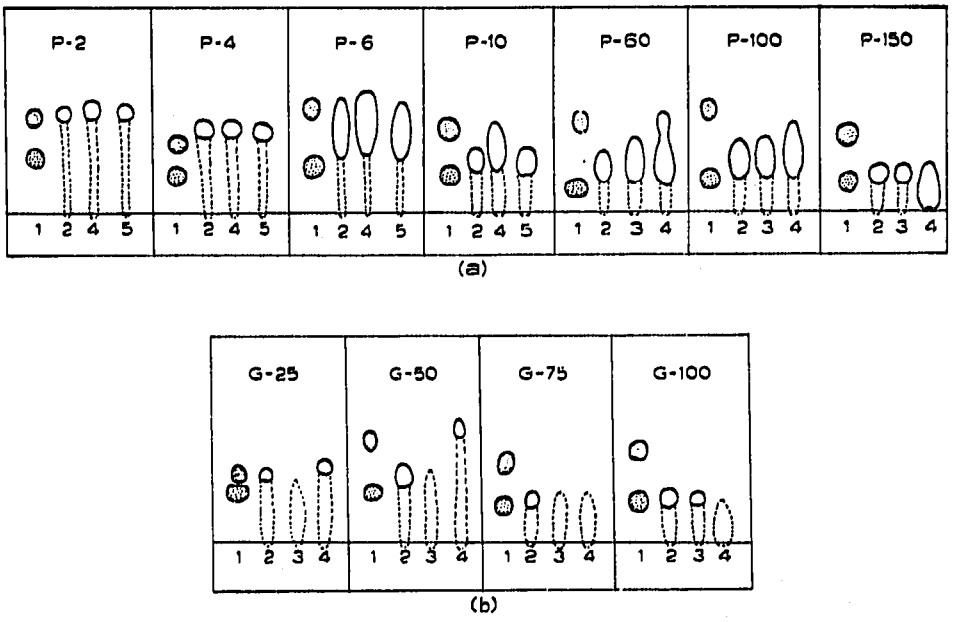

Fig. 2. Chromatograms obtained with 0.5 *N* acetate buffer as eluent on thin layers of (a) Bio-Gel polyacrylamide gels and (b) Sephadex G gels. Samples: (1) Dextran Blue 2000 and $Co(NH_3)_6^{3+}$ as reference substances; (2) fresh 0.1 *M* solution of $ZrOCl_2$; (3) solution with OH–Zr ratio = 1; (4) solution with OH–Zr ratio = 1.5; (5) 0.1 *M* solution aged for 60 days.

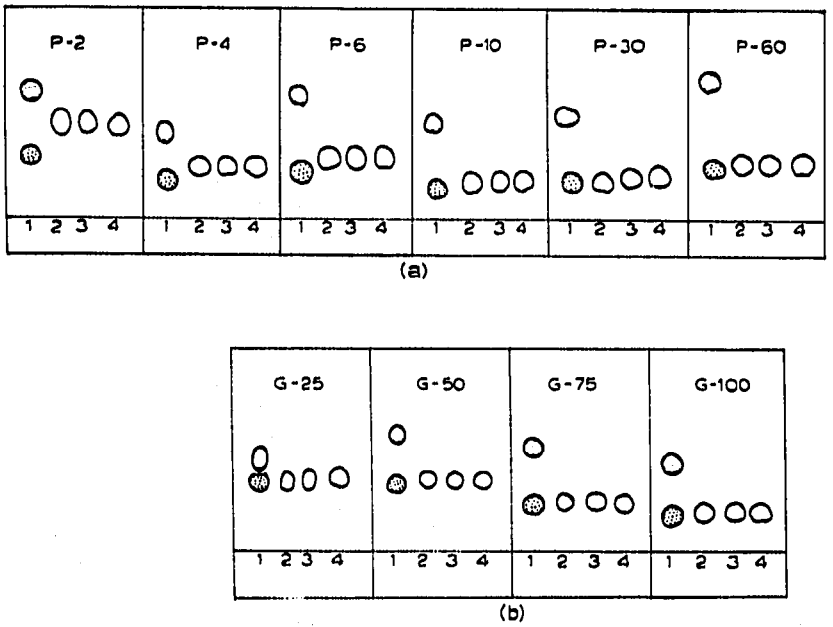

Fig. 3. Chromatograms obtained with 0.5 *N* acetate buffer as eluent on thin layers of (a) Bio-Gel polyacrylamide gels and (b) Sephadex G gels. Samples: (1) Dextran Blue 2000 and $Co(NH_3)_6^{3+}$ as reference substances; (2) fresh 0.1 *M* solution of $Al(NO_3)_3$; (3) solution with OH–Al ratio = 1; (4) solution with OH–Al ratio = 2.

On Sephadex G-50 and Bio-Gel P-60 it can be seen that there are different sizes of polymers, depending on the amount of bicarbonate added, and on Bio-Gel P-6 the elongation of the spots strongly suggests that there is a whole range of sizes of polymeric ions that are being partially fractionated.

A good indication of the size of the polymer can be obtained from the results on the Bio-Gel series because in the gel with the largest pores, P-150, the polymer moves with about the same speed as a monomeric ion.

Al(III). Fig. 3 shows the results obtained with $Al(NO_3)_3$ solution. The chromatogram on Bio-Gel P-2 clearly shows a species intermediate between Dextran blue and a small ion. Larger pore gels, P-4 and P-6, still show some difference, but not the largest pore gels. Aluminium therefore seems to form a rather small polymer and there is no comet formation on the layers.

La(III). No evidence for polymer formation can be observed with $La(NO_3)_3$ solution, as shown in Fig. 4. This does not necessarily mean that no polymeric species are formed, only that they are too small to be excluded by the range of gels tried.

Th(IV). Thorium also shows no evidence of hydrolysis polymers, as shown in Fig. 5.

Ti(IV). Solutions of Ti(IV) yield a spot at the point of origin and a slight spot at the level of the monomer reference ion, connected with a light comet. It seems that the polymers formed are so unstable as to precipitate or so large as to be held back at the point of origin.

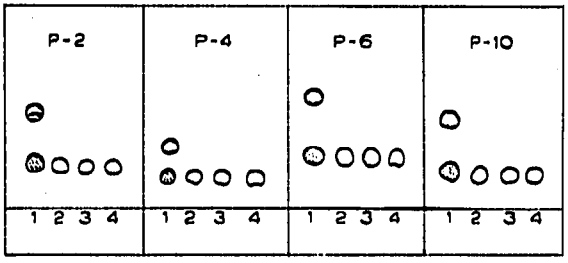

Fig. 4. Chromatograms obtained with 0.5 *N* acetate buffer as eluent on thin layers of Bio-Gel polyacrylamide gels. Samples: (1) Dextran Blue 2000 and $Co(NH_3)_6^{3+}$ as reference substances; (2) fresh 0.05 *M* solution of $La(NO_3)_3$; (3) 0.05 *M* solution aged for 4 days; (4) solution with OH–La ratio = 1.

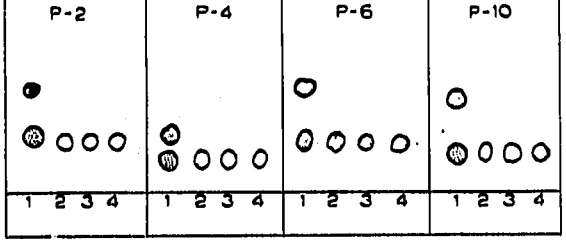

Fig. 5. Chromatograms obtained with 0.5 *N* acetate buffer as eluent on thin layers of Bio-Gel polyacrylamide gels. Samples: (1) Dextran blue 2000 and $Co(NH_3)_6^{3+}$ as reference substances; (2) fresh 0.1 *M* solution of $Th(NO_3)_4$; (3) solution with OH–Th ratio = 1; (4) solution with OH–Th ratio = 2.

Conclusion

The results obtained with the six metal ions show the possibilities of thin-layer gel filtration in the study of hydrolysis polymers. The presence of polymers can be detected in certain electrolyte solutions and a comparison of several ions can give a qualitative picture of the relative size and extent of polymer formation.

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1 J. A. AYRES, *J. Amer. Chem. Soc.*, 69 (1947) 2879.
2 A. M. CHEKMAREV, *Zh. Neorg. Khim.*, 11 (1966) 1480; *Russ. J. Inorg. Chem.*, Vol. 11, No. 6 (1966) 792.
3 S. OHASHI, N. YOZA and Y. UENO, *J. Chromatogr.*, 24 (1966) 300.
4 R. A. HENRY AND L. B. ROGERS, *Separ. Sci.*, 3 (1968) 11.
5 I. KITAYEVITCH, M. RONA AND G. SCHMUCKLER, *Anal. Chim. Acta*, 61 (1972) 277.
6 J. S. JOHNSON AND K. A. KRAUS, *J. Amer. Chem. Soc.*, 78 (1956) 3937.
7 H. M. ORTNER AND O. PACHER, *J. Chromatogr.*, 71 (1972) 55–65.

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