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## Note

### Interactions between hydrolysis polymers of metal ions and other ions in aqueous solution

#### A gel chromatographic study

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The existence of polymeric metal ions in aqueous solutions has been known for many years and their behaviour in various chromatographic systems, especially in ion exchange, has been studied extensively<sup>1</sup>. More recently, the behaviour of such hydrolysis polymers in gel filtration has been reviewed<sup>2</sup> and a survey of metal ions that furnish species separable by gel filtration has been made<sup>3,4</sup>. All of these studies usually concerned the behaviour of a single metal ion in slightly acidic or alkaline media.

In this note, we report some preliminary results on an interesting question that we believe has not been dealt with previously. The hydrolysis polymers are essentially true solutions but with the same groups on the metal ions as the precipitated "hydroxide", and their size ranges from tetramers to polymers with molecular weights of around 30,000. Do such polymers adsorb cations or anions? Also, do they "co-polymerize" with other metal ions which, at the given pH, would be monomers in their absence? These questions, in our opinion, have a fundamental significance in solution chemistry in general, and in separation problems, geological processes and pollution studies (*e.g.*, sea water) in particular. We report examples which, in our opinion, show unambiguously that such hydrolysis polymers can "adsorb" or include both cations and anions.

#### EXPERIMENTAL AND RESULTS

As reported previously<sup>3,4</sup>, a solution of zirconyl chloride ( $ZrOCl_2$ ) in water yields a spot excluded by Sephadex G-10 when developed with 0.1 M sodium acetate-acetic acid buffer (pH 4.70), and also a zone strongly adsorbed on the origin, which is believed to be due to the interaction of the polyhydroxy network of Sephadex with the zirconyl polymer, and an elongated trail between the two, indicating either a range of smaller, only partially excluded, polymers or an adsorption on the Sephadex network. When  $Cr(H_2O)_6^{3+}$ ,  $CrO_4^{2-}$  or  $IO_3^-$  are mixed with a relatively concentrated zirconyl solution, the chromatograms shown in Fig. 1 are obtained.

$Cr(H_2O)_6^{3+}$ , under the same circumstances, would not form a polymer when in solution alone. The lower chromium spots are thus due to two monomers, presumably

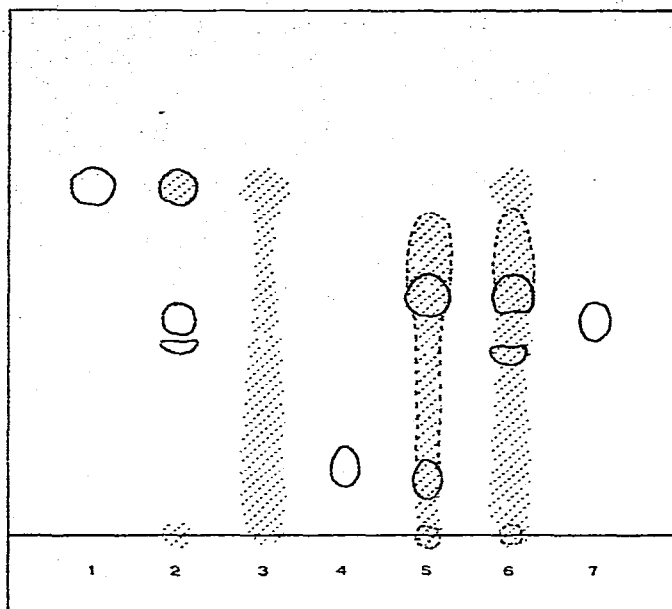


Fig. 1. Thin-layer gel chromatogram of various mixtures of small ions with polymeric zirconyl chloride. Gel, Sephadex G-10; eluent, 0.1 M acetate buffer at pH 4.7. Spots: 1 = Blue Dextran; 2 = 0.4 M  $ZrOCl_2$  heated with  $Cr(H_2O)_6(NO_3)_3$  for 2 h at  $80^\circ$  with a small amount of solid  $NaHCO_3$ ; under the same conditions,  $Cr(H_2O)_6(NO_3)_3$  alone does not form an excluded species; 3 = 0.4 M  $ZrOCl_2$  alone; 4 = 0.1 M  $K_2CrO_4$ ; 5 = 0.1 M  $K_2CrO_4$  mixed with 0.4 M  $ZrOCl_2$  (3:2); 6 = 0.1 M  $NaIO_3$  mixed with 0.4 M  $ZrOCl_2$  (1:2); 7 = 0.1 M  $NaIO_3$ . The shaded zones indicate Zr(IV) as detected with morin. The outlined spots indicate the visible zones for Cr(III) and Cr(VI) and for  $IO_3^-$  the zones revealed with HCl-KI.

the hexaaquo- and a monohydroxo- or monoacetato-chromium species. A purple spot at the same height as the Blue Dextran spot coincides with the excluded zirconium spot shown by spraying with a 0.01% solution of morin in ethanol.

When chromate is added to the zirconyl solution, the chromatogram is more complex. There is a yellow forward trail, showing that some chromate was excluded, then a yellow spot at the point of application and also a spot at the height of the pure chromate (without zirconium). Chromate, when chromatographed alone, is strongly adsorbed to the Sephadex network.

Iodate is not adsorbed on Sephadex G-10 and travels as a small ion at the same speed as hexaaquo-chromium. When mixed with the zirconium chloride polymer, it is found in an elongated trail which, however, does not quite coincide with the zirconyl polymer, some of which travels somewhat further.

## DISCUSSION

The various patterns obtained in gel filtration studies of interactions of polymers with monomers have been reviewed by Wood and Cooper<sup>5</sup>. They showed that a long trail from the spot of the monomer is usually due to a reversible type of interaction; the formation of a distinct zone of the monomer which corresponds to

the zone of the polymer indicates in many instances the formation of a very strong or irreversible association.

In our study, we seem to have examples of all possible types: Cr(III) seems to be strongly associated with the zirconium polymer, chromate less so but sufficiently to migrate with the totally excluded fraction as well as forming a trail, while iodate does not migrate together with the totally excluded fraction but moves faster than the iodate in absence of the zirconium polymer.

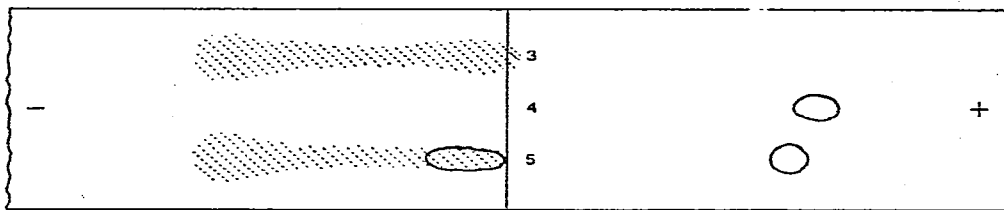


Fig. 2. Paper electropherogram of Zr(IV) and chromate. Paper, Whatman No. 1; Camag high-voltage apparatus; electrolyte, 1 *N* HCl with 500 V at 2.5° for 1 h. Spots: 3 = 0.4 *M* ZrOCl<sub>2</sub> alone (the same solution as in Fig. 1); 4 = 0.1 *M* K<sub>2</sub>CrO<sub>4</sub> alone; 5 = 0.1 *M* K<sub>2</sub>CrO<sub>4</sub> mixed with 0.4 *M* ZrOCl<sub>2</sub> (3:2). The shaded zones indicate Zr(IV) as detected with morin. The outlined spots indicate the visible spots of yellow CrO<sub>4</sub><sup>2-</sup>.

We have also carried out some electrophoretic experiments with the chromate-zirconyl mixture and the results are shown in Fig. 2. Zirconyl solution without the addition of chromate separates into a fast-moving cationic (monomeric?) and a slow-moving (polymeric?) zone joined by a trail. When chromate is present, the slow-moving zone contains some chromate while some chromate also moves anionically with the same speed as a pure solution of chromate.

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