

## Electronic supplementary information

### Does cation dehydration drive the binding of metal ions to polyelectrolytes in water?

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#### Materials

Poly(vinyl sulfate) potassium salt (PVS, stated average molecular weight  $\approx 170\ 000$ ), aluminium (III) and chromium (III) perchlorates from Sigma-Aldrich were of the purest grade available and were used as received. All solutions were prepared in Milli-Q Millipore water or (for NMR) 99.9% D<sub>2</sub>O.

#### *Isothermal Titration Calorimetry (ITC)*

The microcalorimetric unit used in this work, as well as the experimental procedure, have been described in detail in previous work.<sup>1</sup> Briefly, the calorimetric titration experiments consisted of a series of consecutive additions of concentrated aqueous ion solution (HCl, pH=3) into PVS polymer solution (same conditions). The volume of the solution in the calorimetric vessel was 2.6 cm<sup>3</sup> (being either polymer solution or aqueous HCl solution). The titrating solution was added to the calorimetric vessel in aliquots of 8.35  $\mu$ L, from a modified gas-tight Hamilton syringe, through a thin stainless-steel capillary, until the desired concentration range had been covered. The injections were computer controlled. A Kel-F turbine, made in the workshop of Lund University (Sweden) was used throughout, and has proved to promote very good mixing.<sup>1</sup> All experiments were performed at  $308.15 \pm 0.01$  K. The system was calibrated electrically by means of an insertion heater, and the obtained calibration

constant was used to transform the areas of the integrated peaks corresponding to each injection into heat per injection. In isothermal titration calorimetry (ITC) measurements, aliquots of  $\text{Al}^{3+}$  solution (10 mM  $\text{Al}^{3+}$  in HCl (pH=3)) were titrated step-wise into PVS solution contained in the calorimetric cell under constant stirring. The dilution heats were determined separately and used to correct the observed heat in the binding experiment. After performing dilution runs as separate experiments (titration of ion solution into the same aqueous media in the cell to determine the contribution of the dilution of the ions) and titration of aqueous HCl solution into polymer solution (to determine the contribution of the dilution of the polymer) the heats obtained in the binding experiments were corrected for the obtained dilution heats (negative enthalpies of dilution both for the dilution of polymer and the dilution of Al(III)).

#### ***Nuclear Magnetic Resonance***

$^{27}\text{Al}$  NMR spectra were obtained over the temperature range 25-80 °C on a Varian UNITY-500 NMR spectrometer (at 130.248 MHz) using  $\text{Al}(\text{NO}_3)_3$  acidified at pH 2.0 ( $\delta = 0$ ) as external reference and typically, spectral widths of 8000 Hz, acquisition times of 0.5 s, pulse delays of 0.5 s and about 5000 pulses. Studies were also made of second-sphere coordination of PVS (50 mM) and Cr(III) in  $\text{D}_2\text{O}$  solution using  $^1\text{H}$  NMR spectroscopy. Two signals were observed at 1.71 and 4.09 p.p.m., corresponding to the methylene and CH groups of the PVS repeat unit. Indications of outer-sphere interactions were seen through broadening of these resonances upon increasing additions of chromium(III) (up to 2 mM).

#### ***Potentiometric titrations***

For potentiometric titrations, the pH was measured of solutions of the corresponding metal ion alone and in the presence of PVS upon addition of various volumes of standardised solutions of potassium hydroxide. Aqueous solutions of PVS and metal

perchlorates were prepared immediately before titration, and were kept in special polythene flasks. Potassium hydroxide solutions were prepared using Titrisol® solutions and their concentration determined by titration with standard HCl. For the potentiometric titrations, a special glass vessel was used having a double wall, with entries for the glass electrode, calomel reference electrode (Metrohm AG 9100 Herisau), thermometer, tube for circulation of nitrogen and the base of the burette (Metrohm Herisau Dosimat 665). The EMF measurements were made with a WTW pH meter. More details are given elsewhere.<sup>2</sup>

### ***Electrical Conductivity***

Solution electrical resistances were measured with a Wayne-Kerr model 4265 Automatic LCR meter at 1 kHz. A Shedlovsky-type conductance cell, with a cell constant  $0.965 (\pm 0.001) \text{ cm}^{-1}$  was used. Cell constants were determined from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data of Barthel et al.<sup>3</sup> Measurements were taken at  $298.15 (\pm 0.01) \text{ K}$  in a HAAKE Phoenix II P2 thermostat bath. Solutions were always used within 12 hours of preparation. In a typical experiment, 20.0 mL of poly(vinyl sulfate) solution (1 mM), were placed in the conductivity cell; then, aliquots of the chromium(III) or aluminium(III) solutions were added in a stepwise manner using a Metrohm 765 *Dosimate* micropipette. The conductance of the solution was measured after each addition and corresponds to the average of three ionic conductances, with the uncertainty less than 0.2 %. The time necessary to obtain the thermostatic equilibrium and the corresponding electrical resistance values is controlled through home-made software.

1. G. Y. Bai, L. M. N. B. F. Santos, M. Nichifor, A. Lopes and M. Bastos, *J. Phys. Chem. B*, 2004, **108**, 405-413.
2. J. P. R. F. André, H.D. Burrows, C.F.G.C. Geraldes, M.G.M. Miguel, M.H.S.F. Teixeira and L.F. Vilas Boas, *Polyhedron*, 1996, **15**, 4331-4340.
3. J. Barthel, F. Feuerlein, R. Neuder and R. Wachter, *J. Solution Chem.*, 1980, **9**, 209-219.

