Sodium ion interaction with Psyllium husk (Plantago sp.)

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SUPPLEMENTARY INFORMATION

Section I-Streaming potential measurement

Equipment: Muetek Particle charge detector, Metrohm Titrino 702

Reagents: Polydiallyldimethyl ammonium chloride (polyDADMAC) 0.001N working solution prepared from 0.097g of substance in 250ml aqueous solution
Polyethensulphonate sodium (PES-Na) 0.01N solution prepared from 0.0327g of substance in 250ml aqueous solution.

Procedure

Polymer gel was prepared by mixing 0.5g husk and 50ml ultrapure water. The pH was adjusted to 2 and 11 with 1M HCl and 1M KOH respectively. A native pH gel was also prepared using only water. The gel mixtures were left to settle overnight (natural sediment) and the supernatant taken for measurement. Sample supernatant was either undiluted, diluted 1:1 or 1:5 before analysis.

A test run was first carried out to determine charge and estimate titrant volume. For this test measurement, 10ml of sample was measured into the cell. Next piston and pH electrode were inserted, instrument set and the particle charge noted (green led). Manual titration against polyDADMAC was carried out (using a pipette).

Further measurements on other sample aliquots were then run using automatic titration with the Titrino 702.

Section II-Adsorption Isotherm

1. Langmuir Model[i]

Ce/qe=1/qmaxb+Ce/qmax, where Ce= amount of sodium found and qe=amount of sodium bound

Linearised plot of sodium (found/bound) against sodium found gives a slope of 1/qmax, where qmax is the maximum adsorbable.

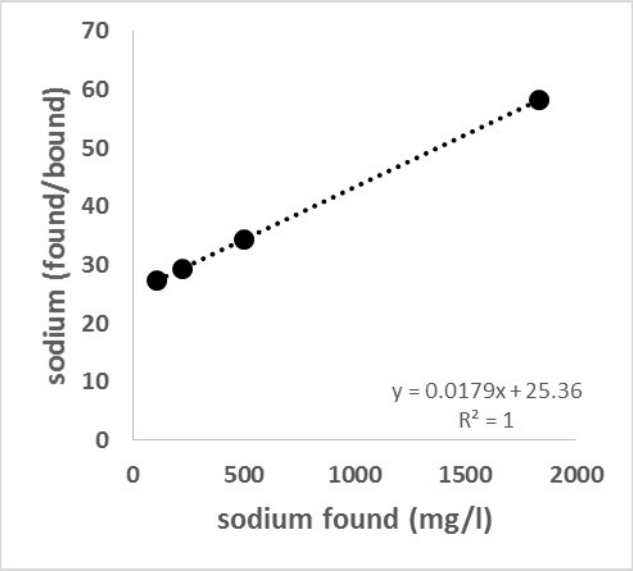

Fig. 1 Langmuir plot of psyllium gel containing sodium at concentrations from 5mg/g to 50mg/g husk.Using the plot, Qmax is calculated at 55mg sodium/g husk

Section III- ^{23}Na-NMR experiments

Low resolution bench top compact Nuclear Magnetic Resonance

In a straightforward free induction decay measurement i.e. a measurement of the response of the system after a pulse and under no external influence such as another magnetic field, the dead time of the spectrometer has an important role to play as it prevents the direct measurement of the FID intensity at time zero. For the low resolution spectrometer used in the present work the dead time was substantial at around 50 microseconds. The measurements made here and shown on figure 5 have t2 values of 208µs and 156µs for the standard sodium solution and the psyllium respectively at a nominal 10% concentration (see Table 1 below)

A long dead time for the probe i.e. a time during which the probe cannot record signal can introduce uncertainty in the measurement of the initial amplitude of the signal. The initial amplitude can be determined either by a simple summation of the NMR intensities over the first few points, or by a fitting procedure whereby the data is fit to a function, normally a Gaussian or exponential, and extrapolated back to time zero. The first method obviously relies on there being no difference between the experimental decay time values. The second method relies on several factors but mainly that the extrapolation is not over too great a range otherwise systematic errors can be introduced.

Using the values for the decay times above and assuming a decay close to exponential, it is calculated that at the times of recording the data (56-72 microseconds) the psyllium signal would be expected to be approximately 6-8% less than the standard due to the more rapid decay. This is sufficiently close to the 10% difference observed in figure 5a (main article) that the conclusion can be drawn that no significant difference in the intensity of signals is observed between the salt solution and the psyllium.

Table 1 shows the measured intensities determined by a) summation of points 6 to 22 microseconds after the dead time delay in the free induction decay, and b) an exponential fit to the free induction decay data.

Sample	(a)Summation intensity	(b) Exponential fit intensity	Exponential fit decay time
Control salt solution 1%	3939	3273	180
Psyllium gel 1%	3985	3387	169
Control salt solution 10%	36780	33904	208
Psyllium gel 10%	32366	29798	156

Therefore further experiments aimed at isolating the coherences due to ordered species, while supressing the central transition were carried out.

Double quantum filtration experiments

The psyllium gel and the salt solution are essentially “liquid like” samples; nevertheless there is a range of mobility in even liquid like samples that can generate different NMR spectra due to the different physical phenomena involved. For the bench top system described above, the only sodium which can be measured is that which is “reasonably” freely tumbling in solution. We will describe what reasonably means shortly. If the motion of the nucleus does not satisfy the condition of freely tumbling, whilst it may be tumbling isotropically, it is outside the region of extreme narrowing of the spectral line. In this case a double quantum filtered experiment can measure those sodium nuclei which are experiencing a restriction in their motion. In actual fact, the satellite lines of the spectral triplet are broadened and this produces a double exponential decay in the normal single quantum FID or equivalently a broadened base in the spectral line. When passed through the double quantum filter the result is two antiphase Lorentzian lines as can be seen in Fig. 5c (main article).

$$\text{IntensityDQ} = A1/(1+[\{x-P1\}/W1]2) - A2/(1+[\{x-P2\}/W2]2) \qquad \text{Equation 1}$$

Further restrictions in motion can produce a population of sodium nuclei which as well as being restricted in isotropic motion, show a quadrupolar splitting due to an anisotropic association with for example a surface. We intend to discuss these issues in more depth in future work. However for now, “reasonably” freely tumbling in solution means the two types of isotropic motions of the sodium nuclei.

As can be seen on figure 5b (main article), a psyllium sample made up in a 2% NaCl solution shows an extremely strong single quantum signal. This is the result of only 128 scans. Figure 5c (main article) shows the result of a carrageenan sample measured using the same double quantum filter as psyllium gels. For psyllium samples however, there is no signal which suggests there is no fraction of sodium outside the freely tumbling region. This is powerful evidence that within the timescale of the NMR experiment there is no fraction experiencing a restriction in motion or “bound” to the psyllium. This is also in agreement with Table 1 (main article) which suggests that the levels of sodium and consequently presumably the corresponding number of binding sites is very low.
The results on figure 5c also suggest that the double quantum filter is extremely effective at removing the single quantum signal. The double antiphase nature of the signal can be clearly seen together with a double Lorentzian fit adjusted such that the areas of each of the Lorentzian functions are equal.

[i] I Langmuir, J. Am. Chem. Soc.,1918 , 40 (9), 1361–1403