

Electronic Supplementary Information 4

Ogston model for the fluorescein dianion probe

Context

The Ogston model of pore size heterogeneity in hydrogels¹ was originally developed to account for observations made in electrically neutral gels, and namely in size exclusion chromatography and gel electrophoresis. Indeed, in both techniques, higher molecular weight, and thus larger, mobile species tend to interact more strongly with the gel, leading to lower partition coefficients respectively lower electric mobility for higher molecular weight. However, the observed cutoff is gradual, spanning a few orders of magnitude of molecular weight from full mobility or partition to complete exclusion or immobility in the gel. This gradual cutoff is incompatible with a homogeneous, static pore size. The Ogston model proposes to address this problem by assuming an effective distribution of pores sizes. The partition or mobility parameters are then obtained by integration over the pore sizes and the associated probabilities.

We use this procedure as well for the charged alginate hydrogels, and integrate the partition coefficients expected for a given pore size over the pore size distribution (eq. 12 in the main text). This greatly improves the fit between experimental data and theory for the macromolecular probe as shown in Fig. 5 in the main text, the curve labeled solid nanochannel (ogston) vs. the curve labeled solid nanochannel (monodisperse).

It is a pertinent question to ask why there seems to be no need to account for the pore size distribution for the low molecular weight probe (Fig. 4 in the main text). Is it that for the fluorescein dianion probe, using the Ogston distribution or simply the mean pore size makes little difference? Or does the Ogston model actually give worse predictions than the assumption of monodisperse pore size distribution? To answer these questions, we evaluated the Ogston model, combined with the Poisson-Boltzmann approach developed here (i.e. eq. 12), also for the fluorescein dianion probe.

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A comparison between the experimentally observed partition coefficients and the model predictions with and without pore size heterogeneity is given in Figure S30. The underlying Poisson-Boltzmann for both cases is the “solid nanochannel model”, described by eq. 1,2, 6-B and 8 in the main text, the difference is either assumption of a single pore size, or integration over a pore size distribution as indicated by eq. 12 in the main text. The nominal pore size itself was calculated for the various concentrations by the best fit equation

indicated in Fig. 3C, with adjustment of the concentration by hydrogel swelling at the given ionic force (Electronic Supplementary Information 3).

Figure S30 shows that applying the Ogston model for the low molecular weight probe has a only a minor effect on the theoretical predictions, indicating that the discrepancy between the solid nanochannel model and the observed partition coefficients is not due to pore size heterogeneity. If anything, the Ogston modification slightly deteriorates the fit.

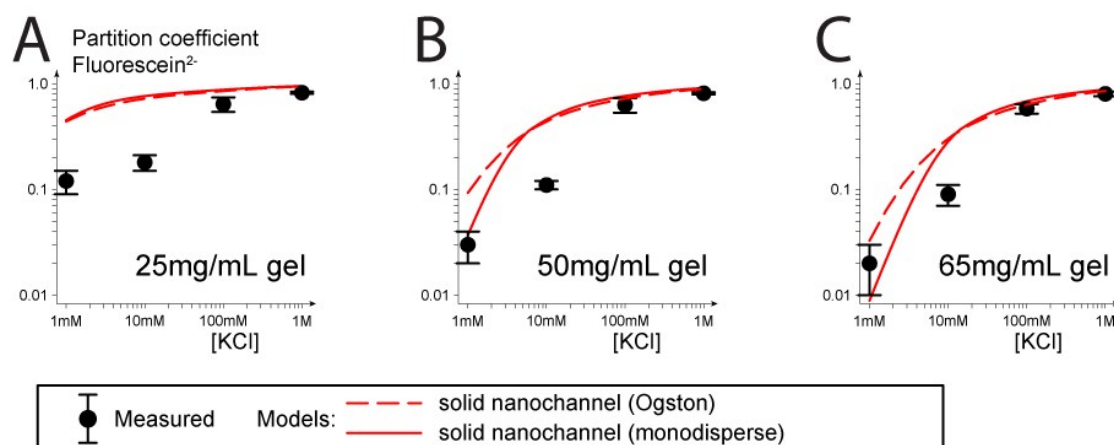


Figure S30. Partition coefficient for the fluorescein dianion as a function of alginate gel concentration and ionic force. The experimentally measured values are taken from Fig. 4 in the main text. The curve labeled solid nanochannel (monodisperse) corresponds to the solid nanochannel model as indicated in Fig. 4 in the main text. The curve labeled solid nanochannel (Ogston) is obtained by eq. 12 in the main text.

Bibliography

1. D. Rodbard and A. Chrambach, *Proc Natl Acad Sci U S A*, 1970, **65**, 970-977.