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Electronic Supplementary Information 2:

Surface effects on the structure and mobility of the ionic liquid C_6C_1ImTFSI in silica gels

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Estimating excluded volume effects on diffusion

Here follows how the Maxwell-Fricke model is slightly altered to include the effect of 'bound' layers that are not totally immobile and then follows how ϕ', *i.e.* the volume fraction of silica plus the volume fraction of 'bound' ionic liquid layers that contribute to the overall excluded volume and p, the fraction of ionic liquid that is mobile, are estimated in fitting our data. The original Maxwell-Fricke model which include effects of bound, immobile layers is:[1,2]

$$D(\phi) = \frac{(1-\phi')D_{\text{bulk}}}{(1+0.5\phi')(1-\phi)}. \tag{1}$$

If the diffusion measured is taken to be an average of two inseparable contributions the above equation alters to:

$$D(\phi) = \frac{pD_{\text{bulk}}}{(1+0.5\phi')} + (1-p)D_{\text{bound}}, \tag{2}$$

where D_{bound} is the diffusion constant for the ionic liquid 'bound' to the silica surface and $p = (1-\phi')/(1-\phi)$ is the fraction of ionic liquid that is not 'bound' to the silica surface.

As ϕ' is a function of ϕ we need to approximate this relation. Assuming that the excluded volume fraction ϕ is made of building blocks with an average size and size distribution that does not change with the ϕ value and that each building block binds the same volume of ionic liquid we can derive that:

$$\begin{aligned} \phi' &= k\phi + \phi = (k+1)\phi, \quad &(3)\\ p &= \frac{1-(k+1)\phi}{1-\phi}, \quad &(4) \end{aligned}$$

where k is a proportionality constant relating the volume of the 'bound' ionic liquid to the volume fraction of silica. Putting equation (3) and (4) in (2) gives the relation:

$$D(\phi) = \frac{(1-(k+1)\phi)D_{\text{bulk}}}{(1-\phi)(1+0.5(k+1)\phi)} + \frac{k\phi}{1-\phi}D_{\text{bound}}. \tag{5}$$

Relating k to amount of 'bound' layers

Equation (5) allows us to fit our data against parameter k. But to be able to interpret k in number of layers 'bound' to the silica surface we have to use equation (3) and make some more assumptions about the surface area available for binding at each volume fraction ϕ. Based on BET surface area measurements we know that most of our ionogels, after having the ionic liquid washed away have a specific surface areas of around 750 m^2/g. Surfaces with different curvature should bind different amount of ionic liquid, but obviously we will not account for this in our qualitative calculations.

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Alternative 1: The straight forward way to use the BET value is to assume that a flat sheet with a a surface area of 750 $\mathrm{m^2/g}$ would give following relation:

$$\phi' = \phi + n a_{\mathrm{IL}} S_{\mathrm{SiO_2}}(\phi), \tag{6}$$

where n is the number of 'bound' ionic liquid layers, a_{IL} is the cubic root of the ionic liquid molecular volume calculated from the ionic liquid density and $S_{\mathrm{SiO_2}}(\phi)$ is the silica surface at each volume fraction ϕ. Here it is important to point out that $S_{\mathrm{SiO_2}}(\phi)$ is not the same as the BET measured specific surface area for the ionogels which prior to the measurement have had all the ionic liquid washed away from them. Setting equation (6) and (3) together we get that

$$n = \frac{k\phi}{a_{\mathrm{IL}} S_{\mathrm{SiO_2}}(\phi)}. \tag{7}$$

To get rid of the ϕ in the above equation we set $\phi = 1$ and interpret what $S_{\mathrm{SiO_2}}(1)$ would mean. Translating ϕ to fraction of a cubic meter volume would mean that $S_{\mathrm{SiO_2}}(1)$ is the surface area of 1 $\mathrm{m^3}$ of silica which has a specific surface of 750 $\mathrm{m^2/g}$. This would give that $S_{\mathrm{SiO_2}}(1) = 1.65 \cdot 10^9\ \mathrm{m^2/m^3}$. This value in equation (7) together with the fitted value of $k = 1.5$ gives that the amount of 'bound' layers $n = 1.1$.

Alternative 2: An alternative way to calculating the number of 'bound' layers is to assume that the building blocks in the gel are monodisperse and spherical particles with radius $R_{\mathrm{SiO_2}}$ giving following relation:

$$\phi = N_{\mathrm{SiO_2}} \frac{4\pi (R_{\mathrm{SiO_2}})^3}{3}, \tag{8}$$

where $N_{\mathrm{SiO_2}}$ is the number of the $\mathrm{SiO_2}$ particles in the ionogel with radius $R_{\mathrm{SiO_2}}$. Putting equation (8) in equation (3) we get

$$N_{\mathrm{SiO_2}} \frac{4\pi (R_{\mathrm{SiO_2}} + n a_{\mathrm{IL}})^3}{3} = N_{\mathrm{SiO_2}} \frac{4\pi (R_{\mathrm{SiO_2}})^3}{3} (k+1). \tag{9}$$

Solving out n we get:

$$n = \frac{R_{\mathrm{SiO_2}}}{a_{\mathrm{IL}}} ((k+1)^{1/3} - 1). \tag{10}$$

Using the BET result of specific surface area of around 750 $\mathrm{m^2/g}$, we can calculate that $R_{\mathrm{SiO_2}} \approx 2$ nm, which would mean that the amount of 'bound' ionic liquid layer is $n = 0.9$ considering that the fitted $k = 1.5$.

References

1 H. Fricke. A Mathematical Treatment of the Electric Conductivity and Capacity of Disperse Systems I. The Electric Conductivity of a Suspension of Homogeneous Spheroids. *Physical Review*, 24(5):575–587, Nov. 1924.

2 L. Masaro and X. Zhu. Physical models of diffusion for polymer solutions, gels and solids. *Progress in Polymer Science*, 24(5):731–775, Aug. 1999.