Synthesis and Characterization of Sulfonated Polystyrene Networks for the Desalination of Seawater
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Motivation

- in 2005 about 1.1 billion people in the world face insufficient supply of drinking water \[1\]
- desalination of seawater an appropriate tool to overcome this malnutrition

- first desalination approaches based on polyacrylate networks
- possible alternative: polystyrene sulfonate

Theory

- water enters polyelectrolyte (osmotic pressure)
- ions are repelled by polyelectrolyte (Coulomb)
- swelling behavior of polyelectrolytes described by modified Flory-Rehner theory:

\[
Q^5 = - \left[ \left( \frac{i}{2V_u \sqrt{I}} \right)^2 + \frac{(1/2 - \chi_1)}{V_1} \right] V_0 \frac{v_e}{V_0}
\]  

\(i/V_u\) concentration of fixed charges in the unswollen polymer, \(I\) ionic strength in solution, \(\chi_1\) Flory-Huggins parameter, \(V_1\) molar volume of the solvent, \(v_e/V_0\) cross-linking density

Synthesis

Degree of Sulfonation

- determined by IR spectroscopy and elementary analysis
- peak a – sulfonate group (S=O stretch vibration)
- peak b – polymer backbone (C-H stretch vibration)

- average of 5 measurements
- ratio a/b linear
- good agreement with Lambert-Beer

\[
\log \left( \frac{I}{I_0} \right) = c \varepsilon d
\]

$I/I_0$ normalized intensity, $c$ concentration, $\varepsilon$ extinction coefficient, $d$ distance

comparison peak ratio a/b to elementary analysis
Swelling Experiments

- sulfonated polystyrene swollen with 1 wt.% NaCl solution
- degree of swelling $Q = \frac{m_{\text{water}}}{m_{\text{polymer}}}$
- slope B of 0.84 showed decent agreement with Flory-Rehner theory
- lower degrees of swelling than polyacrylic acid
- higher dependency on degree of cross-linking

![Graph showing degree of swelling vs. degree of cross-linking for sulfonated polystyrene and polyacrylic acid]
Desalination – Hydrogel Process

- absorption of large amounts of aqueous solution in hydrogel, e.g. polystyrene sulfonate PSS
- external electrolyte is repelled by the charged polymer
- realization in a 3-step process
Desalination – Idealized Run

salt concentration vs. squeezed volume during desalination process

- hydrogels swollen over night with 1 wt.% NaCl solution
- m(swollen polymer) = m(supernatant phase) = 0.5 m(total)
- degree of cross-linking, sulfonation and neutralization were varied
- occupied surface below $c_0 = 1$ wt.% NaCl represents salt reduction in mg
Desalination

- desalination up to 35 %
- higher degree of cross-linking
  $\Rightarrow$ higher salt repulsion
  $\Rightarrow$ worse total salt reduction
Desalination

- better salt repulsion of PAA
- comparable desalination of DC1 PAA and DC0.3 PSS
- best results of PAA with high DC, best results of PSS with low DC

Conclusions

- sulfonated polystyrene networks synthesized and characterized
- degree of cross-linking was varied
- desalination of 1 wt.% NaCl up to 35 %
- lower salt repulsion and degree of swelling than polyacrylic acid
- comparable degree of desalination
Control of Pore Size Distribution in Hydrogels

→ System: A  B  C

<table>
<thead>
<tr>
<th>property</th>
<th>randomly cross-linked</th>
<th>quasi-model [7]</th>
<th>model - SFB 1176</th>
</tr>
</thead>
<tbody>
<tr>
<td>elastic chains</td>
<td>broad size distribution</td>
<td>defined length</td>
<td>defined length</td>
</tr>
<tr>
<td>cross-link functionality</td>
<td>(fixed)</td>
<td>not fixed</td>
<td>fixed</td>
</tr>
<tr>
<td>pore size distribution</td>
<td>broad</td>
<td>middle</td>
<td>small</td>
</tr>
</tbody>
</table>

better defined system
more homogenous mesh size distribution

Thank you for your attention