



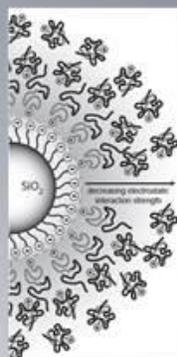
Simulations of Na⁺ Impurities in Nanoscale Ionic Materials

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Abstract

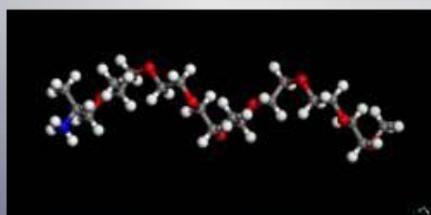
Due to the intriguing properties of the inorganic-organic structures of nanoscale ionic materials (NIMs), these materials can be used in a number of different applications. They can be designed to act as liquids at room temperature without solvents being present and have no volatile organic content. Properties of the NIMs have been shown to change along with the material's structure or environment, necessitating research into how exactly the NIMs changes. The effect of ionic impurities within NIMs, which consists of a positively charged canopy and a negatively charged corona, is investigated in this project. Recently, NMR investigations have revealed that the diffusion of NIMs is dependent on the concentration of ionic impurities, such as sodium ions.



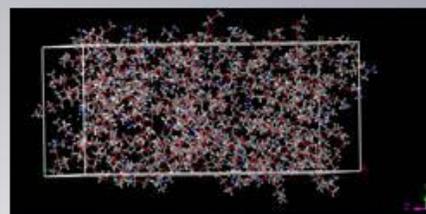
Watan, S. C. et al. J. Am. Chem. Soc. 2006, 128, 11074-11078.

Above: Liquid-like properties of NIMs at room temperature.

Left: Typical NIMs structure with a silica core, sulfonate corona, and an ionic liquid canopy.



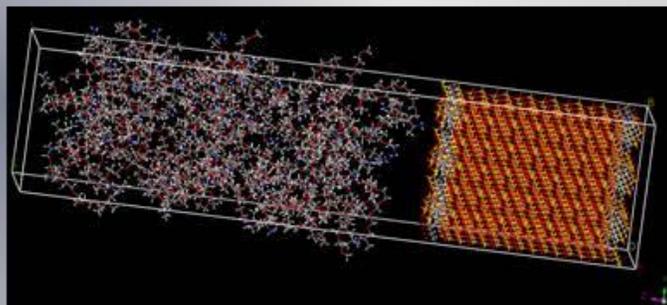
Left: Copolymer of ethylene oxide and propylene oxide in 6:2 monomer ratio used in the formation of the canopy. Each copolymer chain was capped at the propylene oxide end with a positively charged alkyl ammonium group.



Right: Amorphous cell containing 72 canopy chains, 72 sodium ions, and 72 chloride ions.

Right: NIMs structure constructed by layering the canopy chains above the corona and silica surface. The amorphous cell was minimized to reduce close contact between atoms. The AC was then layered with the silica surface and the system was equilibrated using NVT dynamics.

Once the system was sufficiently equilibrated under NVT conditions, it was switched to NPT dynamics for the collection of diffusion data.



All structures were built using Materials Studio Ver. 5.5 GUI and all minimizations and equilibrations were conducted using the Discover Simulation Engine and the COMPASS force field.

NMR Data

Na:SO ₂	D @ 323K (cm ² /sec)
1:1	1.3E-08
0.5:1	4.6E-09
0.11:1	f: 3.3E-08; s: 1.6E-09
0.1:1	f: 3.2E-08; s: 1.4E-09
Mg: 0.5:1	1.4E-08
Bulk M2070	5.3E-08

Data from: M. L. Jespersen, P. A. Mireau, and R. A. Vaia

Table depicting the changes in the diffusion coefficient of NIMs due to changes in sodium ion concentration.

Conclusions

Due to the electrostatic nature of the interaction between the corona and canopy, charged particles such as the sodium ions can change the macroscopic properties and dynamics of the NIMs. As can be seen in the table to the left, increasing the concentration of sodium ions leads to an increase in the diffusion coefficient of the canopy chains, as well as a switch from two distinct diffusion regimes to a single distribution. The sodium ions essentially screen the electrostatic interactions between the corona and the canopy, allowing the canopy to diffuse at a much faster rate. The exchange rate between the canopy particles close to the corona surface and the canopy particles further away is likewise increased by the presence of ions, leading to the change of two diffusion regimes to one.

Acknowledgements

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