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Unique molecular sponges for liquid separation

Researchers separate molecular mixtures by selectively absorbing larger molecules over smaller ones into nanoscale pores using a process driven by depletion force

Collaborative research between Kyushu University and Keio University sheds new light on a mechanism to separate molecules by selectively soaking them up in the nanoscale pores of a plastic-like film. Most peculiar of all? These molecular sponges actually prefer to absorb larger molecules than smaller ones.

When using pores for separating liquids, the focus is often on having the pores the right size to let only small particles through while filtering out the large particles. However, in this case, the researchers used the pores in their films to soak up the larger molecules.

"While one might think that the small molecules will penetrate more easily and be better absorbed by the film, extremely small pores can actually prefer to absorb the larger molecules," commented the authors of the paper announcing the results in the journal *Langmuir*.

The researchers made thin films with nanoscale pores from a relative of common plastics called isotactic poly(4-methyl-1-pentene) and then submerged the films in mixtures of normal alkanes—straight chains of carbon atoms with hydrogen atoms attached to their sides—having different lengths.

Even when the liquid mixtures contained equal volumes of long and short molecules, the films absorbed much larger amounts of the long molecules. Because of the similarity of the molecules, this cannot be explained by a chemical attraction between the film and molecules, and the longer molecules will even replace shorter molecules previously absorbed by the film.

Instead, the researchers explained the absorption based on a mechanism termed depletion force, which arises because of something called entropy. From a physics standpoint, the mixture wants to move to a condition that can increases entropy, which can be thought of as the number of configurational patterns for the molecules.

By trapping the longer molecules instead of the shorter ones in the film, there is effectively more space for the shorter molecules to move around, creating more possible configurations for the molecules.

However, one key for this to work is that the pore size has to be extremely small. Also, while this absorption phenomenon has already been demonstrated in a type of polystyrene, the

films used in this research were even more selective.

With continued development, these unique types of molecular sponges may one day offer new methods for separating chemicals, and a better understanding of the mechanism may also give hints into biological processes such as molecular recognition.

For more information about this research, see "Confined space enables spontaneous liquid separation by molecular size: Selective absorption of alkanes into a polyolefin cast film," Ayano Chiba, Akio Oshima, and Ryo Akiyama, *Langmuir* **35**, 17177 (2019), https://doi.org/10.1021/acs.langmuir.9b02509

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