Pressure Effects on the Dewetting Behaviors of Deep-Cavity Cavitands
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Introduction
Cavities are supra-molecular host molecules with a bowl-shaped-like cavity that allows them to bind guests in 1:1, 2:1, 2:2 as seen in Figure 1. Cavities can also form larger complexes such as hexamer and tetramer structures. The composition and conformation of the rim of the cavity greatly affects the behavior of the cavitand, particularly in its dewetting properties. The hydrophobicity of the pocket also causes the cavitand to behave as a molecular scale nonporous surface. The effects of dewetting are important in the further development of cavities for new separation techniques, nanoscale reactors, and as a probing tool in protein chromatography.

The dewetting effect follows that if the contact angle- the angle formed by the tangent of the droplet with the surface- is larger than 90°, then the surface is hydrophobic while if the contact angle is less than 90° then the surface is considered to be hydrophilic and is considered wetted.

Simulation Methods
In the molecular simulations of the deep-cavity cavitations, the package GROMACS 5.1.3 was used. TIP4PEW model was used to simulate water and general amber force field (GAFF) was used to simulate the cavitations. In the simulations, the cavitands MEMOA, DEMOA, Tri-EMOA, TEMOA, TEXMOA, TEMOA-OH, and TEXMOA-OH were held at a constant temperature of 298.15 K. The system was simulated under a range of pressures from -500 bar to 2500 bar in 500 bar increments, and 1 bar was used in place of 0 bar. The simulation of the cavitand included 3000 water molecules. The net charge of each cavitand was set to be -6e due to six of the eight carboxyl groups being deprotonated to match the expected protonation state at pH 7. Six sodium ions were included in the simulation to neutralize the host charge.

Cavitand Studies

The Methyl Effect
Increasing the methylation of the rim increases the hydrophobicity of the cavitand and decreases the likelihood that water will be found in the cavitand at any given moment. As methyl groups are added around the rim of the cavitand in place of hydrogen, the relative bulkiness of the methyl group narrows the mouth of the cavitand creating a smaller gateway for the water molecules in addition to the hydrophobic effect of the interactions between water and the methyl group.

The Hydroxyl effect
The addition of hydroxyl groups to the rim of the cavitand increases the likelihood that water will be found in the cavitand. The hydrophilicity of the hydroxyl groups attracts water to the mouth of the cavitand and thus increases the likelihood that water will find its way into the belly of the cavitand.

Conclusions
By varying the functional groups located on the rim of deep-cavity cavitand OA, we were able to determine that the methylation of the rim increases the hydrophobicity of the cavitand while also decreasing the average number of water molecules present and the likelihood that water will enter the cavitand. We also concluded that the addition of hydroxyl groups to the rim of the cavitand will increase the number of water molecules present while increasing the likelihood water will enter the cavitand.

References

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