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Hydrophobic Encapsulation of Hydrocarbon Gases

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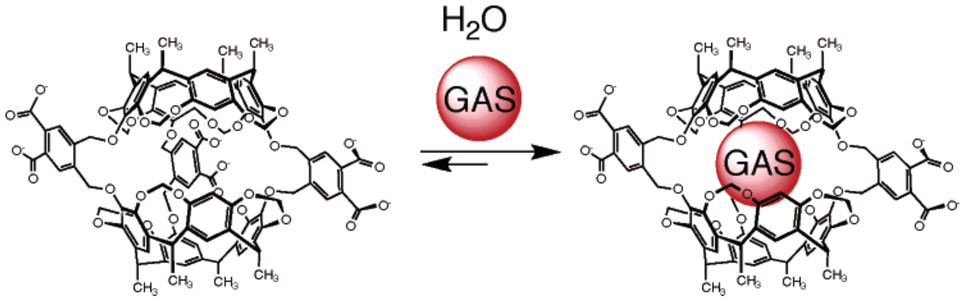
ABSTRACT



Encapsulation data for hydrophobic hydrocarbon gases within a water-soluble hemicarcerand in aqueous solution are reported. It is concluded that hydrophobic interactions serve as the primary driving force for the encapsulation, which can be used for the design of gas-separating polymers with intrinsic inner cavities.

Encapsulation of molecules and ions in the inner spaces of cavitands, (hemi)carcerands, and self-assembling capsules is well documented.[1] Much less is known about encapsulation of gases.[2] As a result of their small size, gases require a higher degree of molecular design. Often, an individual, case-by-case approach is needed, which is based on the specific properties of each particular gas. At the same time, one of the *general* driving forces for gas encapsulation may be solvation. In this Letter, we report on the use of hydrophobic forces for entrapment of gases in water and demonstrate that hydrophobic cavities may encapsulate gases even without intrinsic affinity toward them. Many industrially important gases, such as natural hydrocarbons and haloalkanes, and anesthetic gases, including nitrous oxide and fluorocarbons, are hydrophobic. At the same time, their applications involve water.

To simply illustrate the concept, we used commercially available hydrocarbon, natural gases,[3,4] and traditional hosts, hemicarcerands. In modified Cram hemicarcerands **1** and **2** (Figure 1), two lipophilic resorcin[4]arene hemispheres were connected by three *o*-xylyl bridges. In contrast to known tetrakis-*o*-xylyl bridged hemicarcerands,[5] which require high (≥100 °C) temperatures for guest entrapment and exchange, our design allows for unrestricted encapsulation and movement of solvent and gas molecules in and out. This is due to the remaining gap of ~4 × 7 Å between the two hemispheres, which is quite wide compared to the kinetic diameters[6] of the C_1-C_4 hydrocarbon gases (3.8−4.3 Å).

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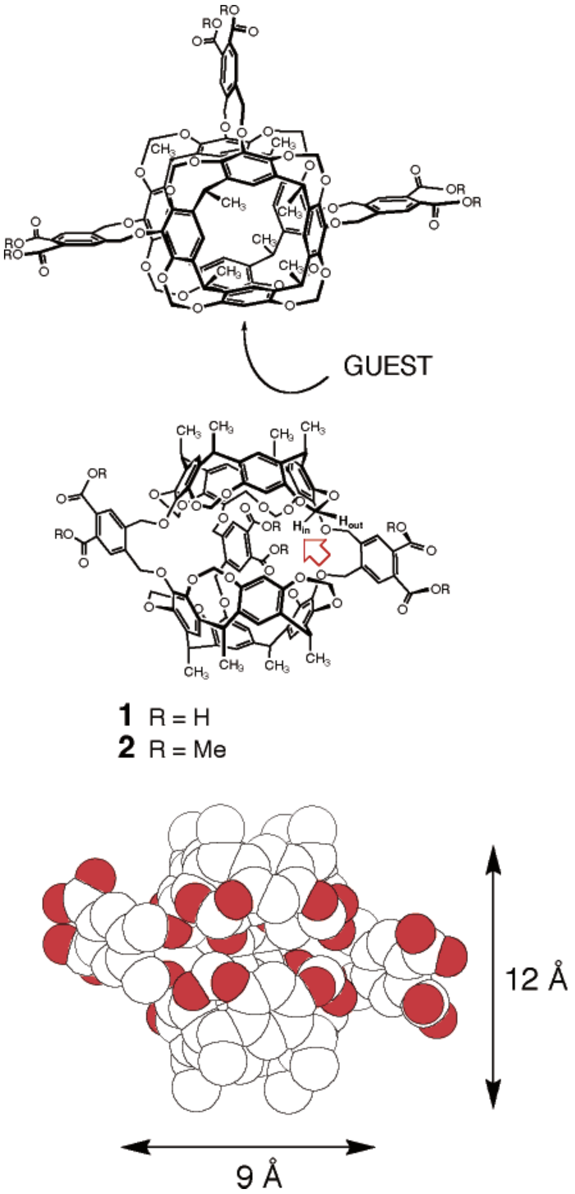

Figure 1. Hemicarcerands **1** and **2**, side and top views. Below: space-filling model of **1** (MacroModel 7.1; MMFs). The gap of ~4 × 7 Å between the two hemispheres is pointed toward the reader.

The lipophilic inner cavity in **1** and **2** is ~12 × 9 Å, large enough to accommodate a xylene-size guest. Despite the structural similarity, hemicarcerands **1** and **2** differ in their solubility. Hexaester **2** is well-soluble in most organic solvents. Derived from **2** by saponification, hexaacid **1** is soluble in water upon addition of a base.[7] This feature allows comparison of the encapsulation of gases by the same cavity in apolar solution and water.

Hexaester hemicarcerand **2** did not encapsulate methane, ethane, propane, or butane in $CDCl_3$ and $(CDCl_2)_2$. No ^1H NMR spectral changes were detected, even when a large excess of gas was used. Apparently, the guests and solvent freely move in and out of the cavity though the widely open portal. With minimal intrinsic (CH-π, van der Waals forces) attraction and constrictive binding,[8] only very weak hemicarceplexes of **2** with gases formed, if at all.

The situation was different in aqueous solution. Water-soluble hemicarcerand **1** clearly demonstrated affinity toward hydrocarbon gases (Figure 2). When a D_2O solution (pH 9.0, NaOD) of **1** was saturated with methane, ethane, propane, or butane, the corresponding hemicarceplexes **1**·gas formed. In the ^1H NMR spectra, the eight inward-facing protons of the OCH_2O bridges (H_{in} in Figure 1) appeared to be most sensitive to the gas presence in the cavity (Figure 2). In empty **1**, these protons were seen as a multiplet at ~4.1 ppm, and they shifted up to 0.2 ppm upfield upon encapsulation. Moreover, in **1**·ethane, **1**·propane, and **1**·butane, they appeared as two doublets at 4.0 and 3.9 ppm (Figure 2C−E).

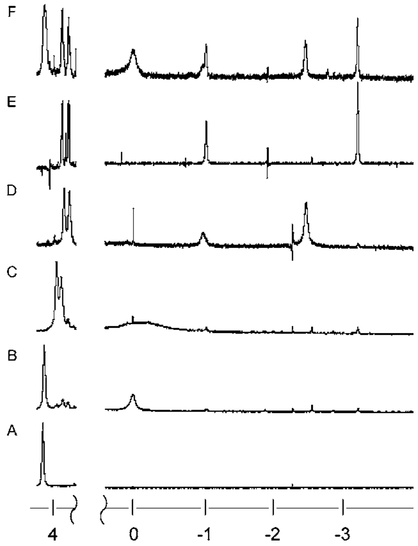

Figure 2. Selected portions of ^1H NMR spectra (500 MHz, D_2O, NaOD, pH 9, 23 ± 1 °C) of (A) hemicarcerand **1**; (B) **1**·methane; (C) **1**·ethane; (D) **1**·propane; (E) **1**·butane (E); (F) complexes of **1** with "in-house" natural gas. The encapsulated guest signals are situated upfield from 0 ppm. The inward-facing protons of the OCH_2O bridges are seen at ~4 ppm.

For all gases, the signals of encapsulated molecules were clearly seen in the upfield part of the ^1H NMR spectra, which indicates a slow exchange process on the NMR time scale (Figure 2, Table 1). Integration of the NMR signals showed a 1:1 stoichiometry in all cases. This also allowed us to obtain the packing coefficients (PC), the ratio of the guest volume to the host volume (Table 1).[9] With the inner cavity of ~160 Å^3, the obtained PC are 18%, 28%, 39%, and 49% for **1**·methane, **1**·ethane, **1**·propane, and **1**·butane, respectively.

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Table 1. Chemical Shifts (ppm), Molecular Volumes (Å^3), and Packing Coefficients (PC, %) for Hydrocarbon Gases and Their Hemicarceplexes with Host **1**[a]

gas	δ (free)	δ (complex)	volume	PC
methane	0.16	−0.01	28	18
ethane	0.81	−0.19	45	28
propane	1.29, 0.87	−1.06, −2.60	63	39
butane	1.30, 0.90	−1.12, −3.37	79	49

[a] In NaOD−D_2O, pH = 9, 23 ± 1 °C. All experiments were performed at least in duplicate, showing good reproducibility.

This is lower than the average 55% value observed for encapsulation of organic guests in solution,[9] but in agreement with the accepted molecular crystallography knowledge for gases.[10] Similarly low values for gas encapsulation were also observed by others.[11,4a,g]

The guest size appears to be an important factor influencing the binding strength, so in addition to hydrophobic effects, CH-π and van der Waals forces are also at play. For larger propane and butane, the signals of free and incarcerated molecules were seen separately, which indicates slow exchange processes on the NMR time scale and also high exchange barriers (Table 1 and Supporting Information). For example, signals for free butane in D_2O are situated at 1.30 (CH_2) and 0.90 (CH_3) ppm, whereas for the encapsulated species they are seen at −1.12 (CH_2) and −3.37 (CH_3) ppm. Such a significant difference in chemical shifts implies that the guest is aligned along the long north−south axis of **1**, and the alkyl protons appear under the shielding power of the resorcinarene aromatic rings. On the ^{1}H NMR time scale, no rapid rotation of the guest around the east−west axis occurs. On the other hand, when smaller methane and ethane were bubbled through the solution of **1**, faster in-and-out exchange processes were observed. For example, with methane a broad peak centered at ~0 ppm appeared, which might represent the averaged chemical shift of free gas (0.16 ppm) in water and the value of its encapsulated species (Table 1). With ethane, an even broader, gently sloping peak at −0.19 ppm was seen. While the gas alkyl protons still appear to be somewhat shielded by the cavity aromatic rings, on the ^{1}H NMR time scale rapid rotation of the guest around the north−south and east−west axes most probably also takes place.

Methane, ethane, and propane easily replace each other in the inner cavity. For example, by flushing hemicarceplex **1**·propane with methane or ethane, the corresponding complexes were generated, and yet, once propane was introduced again, complex **1**·propane was restored. These transformations were repeated a number of times, giving reproducible results. Such exchange cycles cannot be easily achieved in conventional encapsulation studies with liquid and solid guests. At the same time, hemicarceplex **1**·butane is very robust. The butane release requires high temperature (≥100 °C) and vacuum. The complex can even be precipitated by acidification of the parent basic solution and then kept as a solid in the open air for several days.[12]

Another interesting observation was made when the “in-house”, laboratory natural gas (from Atmos Energy) was applied. The gas contains 94.1% methane, 3.1% ethane, 0.8% propane, and 0.2% butane. After 10 min of bubbling, a roughly 2:1:1 mixture of hemicarceplexes **1**·methane, **1**·propane, and **1**·butane was detected by ^{1}H NMR spectroscopy (Figure 2F). This indicates that hemicarcerand **1** binds propane and butane ~60 and 240 times stronger than methane. If the bubbling was continued longer (1 h), only the **1**·butane hemicarceplex was seen. Such selectivity could potentially be used for fine purification of natural gas and biofuels, where high purity methane is needed.

Comparing the data for hemicarcerands **1** and **2** in aqueous and apolar solution, we conclude that hydrophobic interactions served as the *primary* force leading to encapsulation of hydrophobic gases in water. Water molecules can occupy hemicarcerands,[13] but they are most probably excluded during encapsulation. We feel that our findings are quite general and can be used in the design of molecular containers for a variety of hydrophobic gases. The obtained results may also be useful in explaining the mechanisms of biological trafficking of gases and anesthesia. Our immediate goal, however, is separation, purification, and storage of gases. While a number of water-soluble molecular containers for hydrophobic gases are known,[4a,14] they are formed via self-assembly and thus are stable only under specific, rather mild conditions. In contrast, hemicarcerands are robust. In fact, the water solubility of materials with intrinsic hydrophobic cavities is not even needed to encapsulate hydrophobic gases. In a preliminary experiment, powdered host **1** was simply suspended in pure water (pH ~ 7) and flushed with butane over 30 min. As a result, ~40% of complex **1**·butane was formed, implying that hydrophobic cavities may entrap gases even at the water-solid interface.[15]

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Supporting Information Available: Experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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