THE ROLE OF HYDROPHOBIC INTERACTIONS FOR THE FORMATION OF GAS HYDRATES

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ABSTRACT

It is well known that water molecules at room temperature tend to form ‘iceberg’ structures around the hydrocarbon chains of surfactant molecules dissolved in water. The entropy reduction (times the absolute temperature T) associated with the iceberg structure can be considered as the net driving force for self-assembly. More recently, many investigators measured long-range attractive forces between hydrophobic surfaces, which are likely to result from structuring of the water molecules in the vicinity of the hydrophobic surfaces. Similarly, the hydrophobic nature of most gas hydrate formers may induce ordering of water molecules in the vicinity of dissolved solutes. In the present work, the surface forces between thiolated gold surfaces have been measured using an atomic force microscope (AFM) to obtain information on the structure of the thin films of water between hydrophobic surfaces. The results have been used to develop a new concept for the formation of gas hydrates.

Keywords: hydrophobic solute, AFM, hydrophobic force, water structure, hydrate formation

INTRODUCTION

The hydrate formation process remains largely unknown despite a number of hypotheses that have emerged to explain the hydrate nucleation process. The difficulty in addressing this fundamental problem is the lack of concrete evidence for the water molecules around the hydrophobic solute such as methane and the nucleation process leading to the clustering that induces hydrate growth. The most accepted hypotheses on hydrate nucleation involve labile clusters [1-4] and local clustering [5-6]. In the former, hydrate formation is induced by i) the formation of labile clusters upon dissolution of hydrophobic molecules in water, ii) aggregation of these labile clusters to form a hydrate nucleus, and iii) the spontaneous clustering of hydrate nucleus to a critical size that leads to hydrate growth. In the latter, hydrate nucleation is induced by the arrangement of the hydrophobic solute molecules in solution closely resembling the ordering in the hydrate phase. Such a configuration favors the structuring of water molecules, which by thermal fluctuations, leads to the aggregation of hydrate clusters and critical nucleus in the path for hydrate growth.

While there is a continuing debate on the specific molecular events associated with the mechanism for hydrate nucleation, it is evident that the water structure plays a major role in the process. As suggested by both the labile cluster and local clustering hypotheses, the presence of hydropho-

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bic solutes in solution induces the formation of water clusters that are precursors to the hydrate structure. These are either rings structures (pentagons and hexagons) and/or coordination shells comprising of sufficient water molecules to form the basic hydrate cavities.

Liquid water is a dynamic environment of a network of hydrogen bonds between water molecules. The network of hydrogen bonds can be perturbed by thermal fluctuations, and in the case of hydrate nucleation, by the presence of hydrophobic solute molecules.

We present here initial evidence that hydrophobic solutes promote the structuring of water. The results present here are based on the measurement of forces exerted by the water molecules in a confined space between two hydrophobic surfaces using an Atomic Force Microscope (AFM). The results indicate that water molecules tend to reorganize themselves to form ordered structures, which may be related to the nucleation of hydrates, which is often referred to hydrophobic hydration [7].

EXPERIMENTAL

In the present work, the AFM force measurements were conducted between gold substrates hydrophobized by the self-assembly of 1-hexadecanethiol (C₁₆SH). It is well known that n-alkanethiols form stable monolayers with the terminal CH₃ groups in contact with the aqueous phase, providing hydrophobic surfaces whose surface free energy (19 mJ/m²) is lower than any hydrocarbon surfaces studied to date [8]. Further, the strong covalent Au-S bonding provides robust and immobile hydrophobic monolayers, which will preclude the possibility of mobile hydrophobic groups [9,10] or mobile charged patches [11-13] creating the long-range attractive attractions between hydrophobic surfaces.

Materials

A Nanopure II (Barnstead IA) water purification system was used to obtain double-distilled and deionized water with a resistivity of 18.2 MΩ/cm. To remove particulates, a submicron Postfilter (0.2 μm pore size) from Fisher Scientific was used in conjunction with the Nanopure water system. 1-hexadecanethiol (C₁₆SH, 97%) from TCI dissolved in 200 proof ethanol (AAPER Alcohol) was used to hydrophobize the gold surfaces. Sulfuric acid (98%) from VMR International and hydrogen peroxide (H₂O₂, 29.0-32.0%) from Alfa Aesar were used to clean gold plates.

Gold microspheres and gold-coated glass slides were used for AFM surface force measurements. The gold-coated glass slides were obtained by depositing pure gold on glass using a vacuum evaporator. A 50 Å chromium layer was deposited first on the glass prior to coating it with a thin-layer (500 Å) of gold. The chromium coating was necessary to achieve strong bonding between gold and substrate. The coatings produced without the chromium adhesive layer were easily removed in acid solutions.

Gold spheres were produced by melting a gold micro-powder (1.5-3.0 μm, >99.96%, Alfa Aesar) in a furnace. The powder was placed in an alumina crucible, and heated until the temperature was raised above its melting point (1,064.18°C). It was kept at 1,100°C for 15 min and then cooled down slowly. The furnace was flushed with nitrogen to provide an oxygen-free atmosphere. The gold spheres obtained in this manner had a wide range of sizes. Only those with diameters of 15-20 μm were selected for AFM force measurements.

Cleaning Gold Substrates

To obtain high-quality thiol monolayers on gold, a substrate must be cleaned thoroughly prior to immersing it in a thiol solution [14,15]. In the present work, the gold plates were cleaned first by immersing them in a boiling piranha solution (1:2 H₂O₂/H₂SO₄) for 20 min, and then washing it with Nanopure water for 1 min, followed by ethanol wash for 2 min. After the cleaning, a gold plate was immediately contacted with a thiol solution for hydrophobization. The gold plates cleaned in this manner exhibited zero water contact angles, possibly due to the formation of gold oxide (Au₂O₃). After rinsing it with ethanol for 2 min, the contact angle was increased to 65°. It has been reported that the gold oxide is unstable at ambient and can be readily reduced by ethanol [14,15].

For the case of gold spheres, cleaning was done after they had been glued onto cantilever springs. To prevent the glues from being destroyed by the piranha solution, each gold sphere was flushed with ethanol, irradiated by UV irradiation (λ = 254 nm) for 2 hours, and then rinsed with ethanol again.
Hydrophobizing Gold Substrates

The gold plates and spheres cleaned in the manner described above were hydrophobized by contacting them in C_{16}SH-in-ethanol solutions. The kinetics of adsorption varied with the surfactant concentration [16]. In the present work, the hydrophobization was carried out in 10^{-2} or 1 mM C_{16}SH-in-ethanol solutions at room temperature. It was shown that good monolayers can be formed at a concentration as low as 10^{-2} mM, given a sufficient contact time [8]. After the hydrophobization, the gold substrates were washed with ethanol and then dried in a nitrogen gas stream. For a given force measurement, a set of gold plate and sphere was immersed in a thiol solution for a predetermined length of time, so that the hydrophobicity of the two macroscopic surfaces would be the same. A gold sphere was glued onto a cantilever spring before being immersed into a thiol solution. Reversing the order made it difficult to glue the sphere onto a spring.

Surface Force Measurement

Surface force measurements were conducted using a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA) atomic force microscope (AFM) equipped with a standard fluid cell and a scanner “E”. All the AFM force measurements were carried out in a manner described by Zhang et al. [17]. Rectangular non-contact silicon cantilevers (dlevers, Model: 1930-00, Veeco Probes) were used for the force measurements. Their spring constants (k) were determined using the Cleveland method [18]. In each experiment, a gold sphere was glued onto a cantilever with EPON 1004 resin (Shell Chemical Co) using a homemade 3D micromanipulator under an Olympus BH-2 light microscope. The force measurements were conducted immediately after the thiol monolayers were formed on gold substrates.

RESULTS & DISCUSSIONS

Figure 1 shows a force vs. distance curve obtained with a gold sphere and a gold plate hydrophobized in a 0.01 mM C_{16}SH-in-ethanol solution for 10 minutes. The equilibrium contact angle of the gold plate was 105°. The measured forces were net attractive and long-ranged (0–80 nm), with the two surfaces jumping into contact at \( H \approx 22 \) nm. The dashed and dotted lines represent the van der Waals force curves with \( A_{131} = 1.2 \times 10^{-20} \) and \( A_{131} = 2.5 \times 10^{-19} \) J, respectively, while the solid line represents the DLVO theory extended to include the contribution from the hydrophobic force. The force curve was smooth indicating that the long-range attraction was not caused by nanobubbles.

Figure 1b shows the same experimental results plotted in a semi-log plot to show that the long-range attraction can be fitted to a single-exponential force law with a decay length of 35 nm. Thus, the long-range attractive force is shown to decay exponentially, and is much stronger and longer-ranged than the van der Waals forces considered in the present work.
The surface forces measured in the present work and presented in Figure 1 are of very long-range and decay exponentially without steps. Ederth [19] and Ederth et al. [20] also conducted surface force measurements between C_{16}SH-coated gold substrates. Their results also showed long-range attractions, but their force curves showed discontinuities (or steps) at separations in the range of 20-50 nm. They concluded, therefore, that the long-range attractions were caused by the coalescence of bubbles nucleating on the hydrophobic surface. It should be pointed out, however, that Ederth et al. [20] conducted the force measurements after immersing the substrates in 1 mM C_{16}SH-in-ethanol solutions for more than 15 hours. These conditions represented two-orders of magnitude higher thiol concentration and longer contact times than employed in the present work to obtain the results shown in Figure 1.

Figure 2a shows the AFM force measurements conducted in the present work after hydrophobizing the gold substrates under the same conditions as Ederth et al. [20]. The equilibrium water contact angle of the gold plate was 106°. The force curves obtained in water show steps, as reported by these investigators. Figure 2b shows the force measurements conducted after washing the surfaces with appropriate solvents. After hydrophobizing the gold substrates in 1 mM C_{16}SH solution for 12 hours, the surfaces were washed with ethanol and subsequently with pentane, and the residual solvents evaporated off the surface in a nitrogen gas stream. After placing the substrates in a liquid cell, they were washed again by flushing the liquid cell with pure ethanol for a few seconds and subsequently with a plenty of nanopure water. As shown, the measured force was net negative and the force curve was smooth with no steps.

The results presented in Figure 2a and –b suggest that on the gold substrates hydrophobized at a high C_{16}SH concentration (1 mM), multi-layers of thiol are formed, thereby creating a rough surface. The asperities and valleys of the rough surface can trap air bubbles, which coalesce when two surfaces approach each other and give rise to an attractive force. The forces observed under this condition are capillary forces rather than surface forces. The former is much larger than the latter; therefore, the hydrophobic force is easily masked by the capillary force.

The results presented in this communication show that long-range hydrophobic forces are real, and are not caused by preexisting nanobubbles. It is likely that the long-range attraction is caused by the structuring of water molecules in the vicinity of hydrophobic surfaces. It is well known that water molecules form ‘iceberg’ structures around hydrocarbon chains of long-chain surfactant molecules at ambient conditions, which is the basis for self-assembly [7]. One can expect the same to occur around a hydrophobic solute such as methane present in water. Under conditions of lower temperature and high pressure, the structuring of water may be more pronounced, resulting in ice (or hydrate) formation. Further evidence for the structuring of water around hydrophobic surfaces and solutes will be presented at the meeting.

Figure 2. (a) Normalized forces measured in pure water and ethanol/water mixtures between gold surfaces contacted with a 10^{-3} mM C_{16}SH-in-ethanol solution for at least 15 hours; (b) An AFM force curve obtained between gold surfaces immersed in a 1 mM C_{16}SH-in-ethanol solution for 12 hours and then washed with organic solvents before the measurements.
CONCLUSIONS

AFM force measurements were conducted between gold surfaces hydrophobized by self-assembly of 1-hexadecanethiol. When the surfaces were hydrophobized in a 1 mM thiol-in-ethanol solution longer than 6 hours, the force curves showed discontinuities (steps), indicating that the long-range attractions are due to bridging nanobubbles. When the gold substrates were hydrophobized in a dilute (0.01 mM) thiol solution at a relatively short contact time (10 min), a long-range attractive force with a decay length of 35 nm was observed. The attractive force curve exhibited no steps indicating that it was not due to bridging bubbles.

The results obtained in the present work suggest that the hydrophobic force is caused by the structuring of water molecules in the vicinity of hydrophobic surfaces. This conclusion may lead to a new mechanism for the formation of methane hydrates.

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