Supplemental materials

Hydrate-phobic surfaces: Fundamental studies in clathrate hydrate adhesion reduction

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Substrate fabrication, cleaning, and storage protocols

Thiol compounds were purchased from Sigma-Aldrich based on the hydrophobic, hydrophilic and Lewis acid-Lewis base properties of the terminal groups. A 1 mM solution of each thiol was prepared using 100% pure ethanol (VWR) as the solvent. Evaporated gold-coated glass slides (100 nm of gold with a 5 nm adhesion layer of titanium) were purchased from Evaporated Metal Films. Prior to adhesion and contact angle measurements, the slides were rinsed with ethanol and then placed in the thiol solutions for at least 24 h. The slides were then removed from the solutions, rinsed again with ethanol and dried with nitrogen immediately before the measurements. The slides were never exposed to air for longer than 10 min to minimize

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oxidative degradation of the thiols.[1] After contact angle measurements the slides were rinsed with ethanol again and returned to their 1 mM thiol solution to prevent oxidative degradation.

Glass slides purchased from VWR were cleaned by the following protocol: (i) sonication in a 4% by volume solution of Micro-90 detergent (International Products Corporation) in DI water for 15 min, (ii) sonication in DI water for 15 min, repeated twice, (iii) rinsing with DI water between sonications to ensure complete removal of the Micro-90. The cleaned slides were then either stored in DI water until adhesion testing, or they were plasma cleaned and treated with octadecyltrichlorosilane (Sigma Aldrich) by solution deposition or with trichloro (1H, 1H, 2H, 2H-perfluoroctyl) silane (Sigma Aldrich) by vapor deposition in a dessicator at vacuum pressure of -26.5 inHg for 3 hr.

Steel discs purchased from Marv-o-lus Manufacturing were cleaned by scrubbing with acetone and then stored in acetone overnight. The cleaned steel discs were tested directly, or a blend of 80%/20% PEMA/fluorodecyl POSS was deposited on them via spin-coating prior to testing.

It is important to note that surface energy measurements of steel and other metal surfaces vary from study to study because the measured surface energy is highly dependent on organic contamination and cleaning procedures.[2, 3] Our measurements of the surface energy of steel cleaned with acetone (Table S3) are consistent with the values reported by Mantel[3] based on cleaning with acetone.

Surface tension measurements of 19.1% (by weight) THF in DI water solution

The pendant drop method was used to evaluate the variation of the surface tension of the THF-water solution with time due to evaporation of the THF. This variation in surface tension is shown in Fig. S1. The results of the pendant drop experiments were used to approximate the variation of surface tension of sessile drops during THF-water solution contact angle measurements. Based on these measurements, the surface tension of the THF-water solution (initially 19.1 wt.% THF) is initially 47 mN m^{-1} and increases as THF evaporates from the solution.

Advancing and receding contact angle measurements were completed independently within 6 seconds, allowing for no more than ~5% variation in surface tension according to the pendant drop experiments. For advancing contact angle measurements, a 5 μl drop was rapidly output (4 μl s^{-1}) before adding volume at a rate of 0.2 μl s^{-1} and measuring the contact angle. Receding contact angles were measured separately by rapidly depositing a 10 μl drop and then rapidly removing liquid from the deposited drop until the contact line began to recede. The output rate was then reduced to 0.2 μl s^{-1} before measuring receding contact angles.

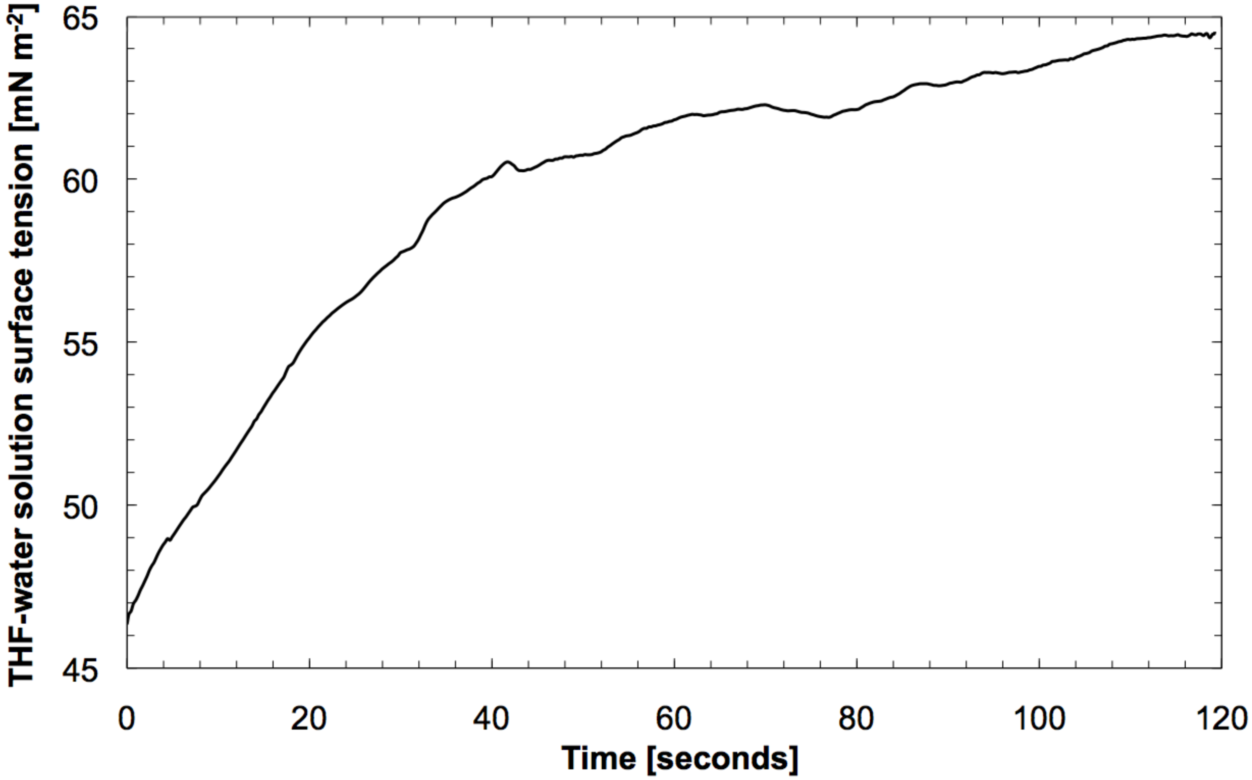

Figure S1. Surface tension measurements of a pendant drop of THF-water solution with an initial concentration of 19.1 wt.% THF in DI water plotted against time. The solution surface tension increases with time due to evaporation of THF from the solution.

Reverse vOCG analysis: Calculation of surface energy parameters of 19.1% (by weight) THF in DI water solution

Van Oss-Chaudhury-Good (vOCG) analysis is conducted by measuring contact angles of at least one nonpolar fluid and two polar fluids.[4] The van der Waals, Lewis acid, and Lewis base parameters of surface energy have been characterized for several fluids. Combining Eq. 1 and 3, one can write:

$$\frac{\sqrt{\gamma_l^{LW}}}{\gamma_l}\sqrt{\gamma_s^{LW}} + \sqrt{\frac{\gamma_l^{+}}{\gamma_l}}\sqrt{\gamma_s^{-}} + \sqrt{\frac{\gamma_l^{-}}{\gamma_l}}\sqrt{\gamma_s^{+}} = \tfrac{1}{2}(1+\cos\theta_{sl}) \qquad \text{(S1)}$$

Where the subscript *l* denotes the test fluid, and the subscript *s* denotes the solid. The surface energies of several test fluids have been previously determined experimentally[5]. Measuring the contact angle of one of the test probe fluids leaves three unknowns in Eq. S1: the van der Waals, Lewis acid, and Lewis base parameters of surface tension of the solid. These unknowns can thus be determined by measuring the contact angles of three test fluids.

The surface energy parameters of liquid 19.1 wt.% THF in water solution are determined using a similar approach, in which advancing and receding contact angles of the solution are measured on three test substrates with known surface energy properties.[6] From Eq. S1 we can write the following matrix equation:

$$\underbrace{\begin{pmatrix} \sqrt{\gamma_{s1}^{LW}} & \sqrt{\gamma_{s1}^{-}} & \sqrt{\gamma_{s1}^{+}} \\ \sqrt{\gamma_{s2}^{LW}} & \sqrt{\gamma_{s2}^{-}} & \sqrt{\gamma_{s2}^{+}} \\ \sqrt{\gamma_{s3}^{LW}} & \sqrt{\gamma_{s3}^{-}} & \sqrt{\gamma_{s3}^{+}} \end{pmatrix}}_{\mathbf{A}} \underbrace{\begin{pmatrix} \sqrt{\gamma_l^{LW}}/\gamma_l \\ \sqrt{\gamma_l^{+}}/\gamma_l \\ \sqrt{\gamma_l^{-}}/\gamma_l \end{pmatrix}}_{\mathbf{x}} = \underbrace{\begin{pmatrix} \frac{1}{2}(1+\cos\theta_{ls1}) \\ \frac{1}{2}(1+\cos\theta_{ls2}) \\ \frac{1}{2}(1+\cos\theta_{ls3}) \end{pmatrix}}_{\mathbf{b}} \qquad \text{(S2)}$$

Then $\mathbf{x} = \mathbf{b} \times \mathbf{A}^{-1}$, where **A** and **b** are known from vOCG analysis and from the 19.1 wt.% THF in water contact angle measurements respectively. The surface tension of the THF-water solution is calculated from the quantities in **x** by rearranging the relation, $\gamma_l = \gamma_l^{LW} + 2\sqrt{\gamma_l^+ \gamma_l^-}$, to obtain $\gamma_l = \dfrac{1}{\left(\sqrt{\gamma_l^{LW}}/\gamma_l\right)^2 + 2\left(\sqrt{\gamma_l^+}/\gamma_l\right)\left(\sqrt{\gamma_l^-}/\gamma_l\right)}$. The individual parameters of surface tension are then calculated by multiplying **x** by the overall surface tension. Advancing and receding contact angles of the THF-water solutions were used with a matrix **A** composed of advancing and receding surface energy parameters respectively. The resulting advancing and receding surface energy parameters calculated for each triplet of test substrates were averaged to obtain an estimate of the actual surface energy parameters of the 19.1 wt.% THF in water solution. The estimated parameters of surface energy for the THF-water solution are provided in Table S1 along with the surface energy parameters of water for comparison.

Justification for fitting adhesion strength versus work of adhesion correlations through the origin

To choose an appropriate fit for plotting adhesion strength of a solid (here THF hydrate) against the work of adhesion a probe fluid we first argue that the work of adhesion, W_{AB}^a, of any probe fluid (A) with non-zero, positive values of $\sqrt{\gamma_A^{LW}}$, $\sqrt{\gamma_A^+}$, and $\sqrt{\gamma_A^-}$ to a substrate (B) can be zero if and only if the adhesion strength of the solid itself on that substrate is zero. This is understood by studying Eq. 1, which is valid for both solids and liquids. For non-zero, positive surface energy parameters, $\sqrt{\gamma_A^{LW}}$, $\sqrt{\gamma_A^+}$, and $\sqrt{\gamma_A^-}$, of a probe fluid, $W_{AB}^a = 0$ implies that the surface energy parameters of the substrate material, $\sqrt{\gamma_A^{LW}}$, $\sqrt{\gamma_A^+}$, and $\sqrt{\gamma_A^-}$, must be zero. Consequently, the work of adhesion of the solid (here THF hydrate) to that substrate must be zero. The net adhesive force between two materials, resulting from van der Waals and Lewis acid-Lewis base interactions, decays monotonically with separation distance. Therefore, W_{AB}^a, which is the integrated dot product of net adhesive force and the separation distance, is zero if and only if the maximum force of separation is zero. It follows that the maximum stress (normal and/or shear), $\tau_{max,AB}$, required to separate THF hydrate from a surface is zero if and only if the work of adhesion to that substrate, W_{AB}^{a}, of any probe fluid having positive values of $\sqrt{\gamma_A^{LW}}$, $\sqrt{\gamma_A^{+}}$, and $\sqrt{\gamma_A^{-}}$ is zero. In conclusion, any physically meaningful fit to data relating adhesion strength of a material to the work of adhesion of any other material must pass through the origin.

Table S1. Surface energy parameters of 19.1 wt.% THF in water solution and pure water at 25˚C, where $\gamma^{total} = \gamma^{LW} + 2\sqrt{\gamma^{+}}\sqrt{\gamma^{-}}$.

Liquid	γ^{LW} [mJ m^{-2}]	$\sqrt{\gamma^{+}}$ [mJ$^{1/2}$ m^{-1}]	$\sqrt{\gamma^{-}}$ [mJ$^{1/2}$ m^{-1}]	γ^{total} [mJ m^{-2}]
19.1 wt.% THF in water solution at 25˚C	18	1.6	9.1	47
Water at 25˚C	21.8	5.05	5.05	72.8

Table S2: Roughness data for clean glass, bare steel, 80/20 PEMA/fluorodecyl POSS on steel, and some representative silanes and thiols. The Wenzel roughness (total surface area/ occluded area) is $r < 1.06$ for all test surfaces.

Substrate	Root-Mean Square Roughness, R_q	Wenzel Roughness, r
Clean glass	0.63 ± 0.1 nm	1.01
Trichloro (1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane	1.82 ± 0.07 nm	1.06
1*H*,1*H*,2*H*,2*H*-Perfluorodecanethiol	2.30 ± 0.07 nm	1.03
Bare steel	0.85± 0.04μm	1.01
80/20 PEMA/fluorodecyl POSS	0.85 ± 0.04μm	1.01

Table S3. Results of the adhesion tests for all test surfaces, along with measured advancing and receding contact angles of DI water and 19.1 wt.% THF in water solution, and calculated advancing and receding surface energy data. More than a four-fold reduction in adhesion strength is observed on 80/20 PEMA/fluorodecyl POSS relative to bare steel.

Substrate	THF hydrate adhesion strength [kPa]	# of tests	Contact angles of DI water [degrees]		Contact angles of 19.1% wt. THF/water solution [degrees]		Total surface energy [mJ m^{-2}]	
	τ		θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}	γ_{adv}	γ_{rec}
Bare steel	422 ± 69	6	72.2 ± 2.1	0	65.0 ± 1.5	0	37	NA
Clean glass	283 ± 82	9	6.5 ± 0.7	0	0	0	51	NA
4-Mercapto-1-butanol	185 ± 39	12	35.0 ± 0.9	5.3 ± 0.9	23.8 ± 0.3	6.4 ± 0.9	52	NA
50/50 1-Butanethiol/ 4-Mercapto-1-butanol	179 ± 45	18	64.2 ± 1.0	34.2 ± 1.0	41.7 ± 1.5	31.6 ± 0.9	48	57
Methyl 3-mercaptopropionate	160 ± 32	11	69.0 ± 1.7	51.8 ± 1.6	49.0 ± 1.0	20.4 ± 3.5	44	50
50/50 Butanethiol/ Methyl 3-mercaptopropionate	149 ± 20	13	82.0 ± 1.4	63.1 ± 2.6	59.0 ± 0.8	48.5 ± 1.3	38	45
Trichloro (1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane	133 ± 15	11	120.8 ± 0.8	90.2 ± 3.3	80.3 ± 1.3	71.2 ± 1.6	8	26
1-Butanethiol	121 ± 48	13	99.5 ± 0.6	86.8 ± 1.0	70.0 ± 1.3	68.0 ± 1.0	30	41
Octadecyltrichlorosilane	114 ± 23	8	112.5 ± 0.6	95.8 ± 0.5	70.8 ± 0.3	64.8 ± 1.9	24	28
1*H*,1*H*,2*H*,2*H*-Perfluorodecanethiol	111 ± 24	8	124.4 ± 1.0	102.4 ± 0.4	89.8 ± 1.4	80.4 ± 0.8	10	24
80/20 PEMA/fluorodecyl POSS	90 ± 16	11	125.0 ± 0.8	115.0 ± 1.2	97.3 ± 0.6	90.0 ± 1.2	9	12

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