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**ADHESION OF ALUMINA SURFACES THROUGH CONFINED  
WATER LAYERS CONTAINING VARIOUS MOLECULES**

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## ADHESION OF ALUMINA SURFACES THROUGH CONFINED WATER LAYERS CONTAINING VARIOUS MOLECULES

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### ABSTRACT

When two surfaces confine water layers between them at the nanoscale, the behaviour of these confined water molecules can deviate significantly from the behaviour of bulk water and it could reflect on the adhesion of such surfaces. Thus, the aim of this study is to assess the role of confined water layers on the adhesion of hydrophilic surfaces and how sensitive this adhesion is to the presence of contaminants. Our methodology used under water AFM force measurements with an alumina sputtered sphere-tipped cantilever and a flat alumina single crystal, then added fractions of ethanol, dimethylformamide, formamide, trimethylamine, and trehalose to water, as contaminants. Such solutions were designed to illuminate the influences of dielectric constant, molecular size, refractive index and number of hydrogen bonds from donors and acceptors of solutes to water. Apart from very dilute solutions of dimethylformamide, all solutions decreased the ability of confined water to give adhesion of the alumina surfaces. The predicted theoretical contribution of van der Waals and electrostatic forces was not observed when the contaminants distorted the way water organizes itself in confinement. The conclusion was that adhesion was sensitive mostly to hydrogen bonding network within water layers confined by the hydrophilic alumina surfaces.

### INTRODUCTION

Many theories have been very successful in describing the adhesion experienced by surfaces, from the macroscale to the nanoscale.<sup>1,2</sup> As highlighted by Israelachvili in the preface of his latest and comprehensive book, in the past two decades the science of intermolecular and surface forces has exploded in many directions, both at the fundamental and applied levels, and into new areas.<sup>3</sup> Recently, nanoadhesion has focused on relating macroscopic adhesion to single adhesive bonds at the molecular level. However, when two surfaces confine water in between them at the nanoscale, the behaviour of confined water molecules usually deviate significantly from the behaviour of bulk water. Molecular dynamics modelling showed that water molecules in between two inorganic single crystals can be squeezed out layer by layer, via the application of an increasing normal force, although the last water monolayer could not be squeezed out, even at pressures where plastic deformation of the single crystals is expected.<sup>4</sup> Major et al. reported a dramatic transition in the mechanical properties of water confined by hydrophilic surfaces with less than 1 nm interfacial separation: the measured viscosity was seven orders of magnitude greater than that of bulk water at room temperature.<sup>5</sup> Their Monte Carlo simulation revealed enhancement in the tetrahedral arrangement of water molecules as well as in the number of hydrogen bonds to surfaces as an explanation for the high viscosity of the confined water. Such observations were corroborated by Jinesh et al. who presented atomic-scale friction force measurements that strongly suggested that capillary condensation of water between a tungsten tip and a graphite substrate led to the formation of ice at ambient temperature.<sup>6</sup> This

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3 phenomenon increased the friction force, introduced a short-term memory in the form of an  
4 elastic response against shearing, and allowed them to “write” a temporary line of ice on the  
5 hydrophobic surface. On the other hand, Raviv et al. observed that the effective viscosity of  
6 water remains within a factor of three of its bulk value, even when it is confined to films in the  
7 thickness range of  $3.5 \pm 1$  to  $0.0 \pm 0.4$  nm by mica surfaces, measured with surface force  
8 apparatus.<sup>7</sup> They argued that in the case of water, confinement seems primarily to suppress  
9 formation of the highly directional hydrogen-bonded networks associated with freezing, so that  
10 the effect of confinement itself is equivalent to a pressure or density increase relative to the  
11 unconfined bulk, due to the attraction exerted on the solvent molecules by confining walls; such  
12 a density increase would oppose any tendency to freeze. The apparent contradiction is explained  
13 by the recent findings from Khan et al. who observed that significant changes in the behaviour  
14 of confined water occurs only in the last 3–4 layers of water molecules.<sup>8</sup> The picture that  
15 emerges is that those measurements from Raviv et al. might not have probed the quasistatic  
16 mechanical properties of the last 3–4 molecular layers.  
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20 This paper attempts to assess the role of confined water on the adhesion of hydrophilic surfaces.  
21 Many examples justify such study: (i) cements are hydraulic binders which inherently confine  
22 water at the nanometric gaps between their hydrating particles,<sup>9</sup> such confined water having an  
23 important effect on the mechanical strength of cementitious materials;<sup>10</sup> (ii) interaction between  
24 proteins and their hydration waters, as proteins are separated on average by 2–3 water layers,<sup>11</sup> is  
25 one of the most complex problems in biophysics, provided small changes in the structure and  
26 dynamical behaviour of the water molecules at peptide–water interface can modify protein  
27 conformation, which, in turn, determines its function;<sup>12</sup> and (iii) sea cucumbers are example of  
28 echinoderms with the ability to rapidly and reversibly alter the stiffness of their connective  
29 tissue, whenever they secrete soluble macromolecules triggered by any threatening condition.  
30 Man-made materials inspired by the ability of sea cucumbers to increase elastic modulus by an  
31 order of magnitude have already been developed, and water acts as a competitive hydrogen  
32 bonding agent in order to control their stiffness.<sup>13</sup>  
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36 The small size and double-donor double-acceptor capacities of water molecules give them a  
37 unique flexibility to form a variety of hydrogen bonds. Confinement tends to distort the way  
38 water organizes itself and so do contaminants, which supposedly affect the role confined water  
39 plays in adhering hydrophilic surfaces. To test this hypothesis, atomic force microscopy (AFM)  
40 was used to probe the adhesion of two alumina surfaces in the presence of water and other  
41 molecules – dimethylformamide (DMF), formamide (FA), ethanol (EtOH), trimethylamine  
42 (TMA), and trehalose (THL) – chosen because of their capability to vary the solution dielectric  
43 constant, solution refractive index, the number of hydrogen bonds from donors and acceptors of  
44 the solutes with respect to water itself, and finally molecular weight ( $M_w$ ) and therefore the size  
45 of the contaminant molecule. First, theoretical predictions of adhesion are calculated using  
46 Derjaguin approximation of a sphere near a flat surface, based on Hamaker constants calculated  
47 with the help of Lifshitz theory. Then, experiments are presented to compare with the theory.  
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### 53 PREDICTED THEORETICAL ADHESION

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55 Generally, the pull-off force ( $F_{ad}$ ) we assess with AFM is a combination of the electrostatic  
56 force ( $F_{el}$ ), the van der Waals forces ( $F_{vdw}$ ), the meniscus or capillary force ( $F_{cap}$ ), and the forces  
57 due to chemical bonds or acid-base interactions ( $F_{chem}$ ):  $F_{ad} = F_{el} + F_{vdw} + F_{cap} + F_{chem}$ .<sup>14</sup> In this  
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study we investigate interaction forces between two fully submerged alumina surfaces which are hydrophilic, chemically inert, and quite neutral in terms of isoelectric point (pH ~ 6 after zeta potential measurements).<sup>15</sup> Therefore, only  $F_{el}$  and  $F_{vdw}$  are present, so that the force interactions could be described by the classical DLVO theory.<sup>16</sup> Concerning the electrostatic forces, we do not expect significant Coulombic charges to build on the surfaces, and therefore we should look at interaction of dipoles, and, thus, dielectric constant of the medium in between the surfaces, as a parameter likely to reproduce their contribution to the overall adhesion. Among the substances we studied, EtOH exhibits a dielectric constant which is one quarter that of bulk water, whilst DMF exhibits a dielectric constant which is half that of the bulk water, whereas the dielectric constant of FA nearly matches that of bulk water. As two chemically identical surfaces were employed in the force measurements, the contribution from van der Waals forces is expected to be attractive, and therefore will increase the maximum adhesive force.<sup>3</sup> As van der Waals forces arise from the dipole field of an atom reflected back by a second atom that has been polarized by such field, the refractive index of the medium separating two surfaces can strongly influence the van der Waals forces between said surfaces. Thus, we used Raju's relations for calculating the dielectric constant of binary mixtures of the liquids and Heller's relations for calculating the refractive indices of our solutions.<sup>17,18</sup> With this in mind, we calculated the Hamaker constants ( $A$ ) on the basis of Lifshitz theory which can be extended to bodies interacting in a medium, according to Equation 1:

$$A = \frac{3}{4} kT \left( \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (1)$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature,  $h$  is Planck's constant,  $\nu_e$  is the main electronic absorption frequency of the system, and  $\epsilon$  and  $n$ , respectively, the static dielectric constant and the refractive index of two identical phases 1 interacting across a medium 3. Our calculations considered the dielectric constant of alumina surfaces as 9.34 and their refractive index as 1.76. Ultimately, for a spherical particle with radius  $R$  distant  $D$  from a flat surface, the Derjaguin approximation, assuming that  $D < R/100$ , leads to the couple of equations below that enable calculations of theoretical free energy ( $W_{th}$ ) and adhesion force ( $F_{th}$ ) of the system under study. Results of AFM experiments, respectively the adhesive energy ( $W$ ) and the pull-off force ( $F_{ad}$ ), can thus be compared to those theoretical ones.

$$W_{th} = -AR/6D \quad (2)$$

$$F_{th} = AR/6D^2 \quad (3)$$

One difficulty associated with AFM force measurements is to estimate the separation  $D$  between the cantilever and the substrate at the contact. To do so, we relied on parallel calculations and comparison to other similar systems. Kendall et al. simulated the contact between two MgO surfaces in presence of water and demonstrated that the stress exerted by the MgO nanoprobe onto the MgO slab in order to squeeze out water molecules from the contact down to the fourth water layer is approximately 1.5MPa.<sup>4</sup> Four water molecules roughly corresponds to a distance  $D = 1$ nm. Considering that the area of effective interaction of our sphere with radius  $R = 2 \mu\text{m}$  at a distance  $D = 1$  nm from the flat surface is given by  $2\pi RD$  and the compressive load applied by our cantilever during its approach to surface of 20 nN, the stress of 1.5 MPa is matched. This is why we arbitrarily adopted the separation between the alumina surfaces in our study as  $D = 1$  nm in order to calculate the theoretical values for adhesion force and interaction free energy.

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3 Further molecular dynamic simulations could better determine the actual separation. With a  
4 separation distance of 1 nm between each other and confining some water layers in between, the  
5 alumina surfaces would likely experience the dominance of forces other than electrostatic and  
6 van der Waals ones.<sup>19</sup> Such dominant forces are often called non-DLVO forces.  
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9 Although most of our AFM experiments were performed in liquid media, we tested the adhesion  
10 of the alumina surfaces in air. The relative humidity (RH) in the laboratory was measured at 25-  
11 35%. According to Deng et al., at a RH of 15%, a monolayer of water molecules adsorbs from  
12 the vapour phase onto the alumina surface and is followed by a second layer of water molecules  
13 at 35-40% RH.<sup>20</sup> If we assume two molecular water layers on each alumina surface of AFM  
14 apparatus, at contact, four water layers are confined within the gap ( $D = 1\text{nm}$ ), sufficient to  
15 develop a capillary force of approximately 27 nN, according to the model proposed by Butt and  
16 Kappl for a sphere ( $R = 2\ \mu\text{m}$ ) interacting with a flat surface (contact angle  $\Theta_1=\Theta_2=75^\circ$ ).<sup>21</sup> This  
17 theoretical capillary force, corresponding to meniscus whose curvatures are given by azimuthal  
18 radius ( $l$ ) of 63 nm and meridional radius ( $r$ ) of 1 nm, will be compared to AFM experimental  
19 results.  
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## 22 23 24 EXPERIMENTAL

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26 AFM measurements were performed using a NanoWizard II AFM (JPK, Germany) whereby the  
27 normal deflection of the AFM cantilever is converted into normal force ( $F_N$ ) as a function of  
28 separation distance ( $D$ ) using the relationship given by Hooke's law,  $F_N = k_N x$  where  $k_N$  is the  
29 cantilever spring constant and  $x$  is the normal deflection of the cantilever. For the sake of clarity  
30 throughout the comparisons, we present the pull-off force and the adhesive energy operating at  
31 the nanoscale of contact between the hydrophilic alumina surfaces. We did not observe any  
32 significant dependence of either pull-off force or adhesive energy as a function of the cantilever  
33 velocity over the range 0.1 to 2  $\mu\text{m/s}$ . Each force measurement was an average of 64 points  
34 probed in an area of 100 x 100  $\mu\text{m}$  onto an alumina single crystal substrate (c-sapphire 0001, 5 x  
35 5 x 0.5 mm, both sides polished (roughness of 0.5nm), Pi-Kem Ltd, UK). The cantilever was  
36 chosen to resemble the large radius of curvature of a typical surface and was developed by  
37 NanoWorld AG (Switzerland) to present a 2.0  $\mu\text{m}$  radius silica sphere at its apex and sputtered  
38 with a 20 nm thickness film of amorphous alumina, exhibiting a nominal spring constant of 0.2  
39 N/m. The system is illustrated schematically in Figure 1, sphere-on-flat geometry system, along  
40 with a typical experimental result for alumina in pure water. Force measurements in liquid  
41 media were performed with both the substrate and the cantilever fully submerged. When  
42 retracting the tip from the substrate surface, the tip stays near to the surface until the force stored  
43 in the cantilever, due to tensile deflection, overcomes the adhesive tip-sample interaction.  
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48 To probe the role of non-DLVO forces on the adhesion of the alumina surfaces, we designed  
49 solutions to illuminate the influences of dielectric constant, molecular size, refractive index and  
50 the number of hydrogen bonds from donors and acceptors of the solutes to water. Aqueous  
51 solutions were thus prepared using dimethylformamide, formamide, ethanol, trimethylamine,  
52 and trehalose. Among these substances, formamide is the simplest available liquid able to form  
53 C=O...H-N type hydrogen bond which is important for studying hydrogen bonding interactions  
54 occurring in hydrated proteins, such as peptide linkages. Table 1 characterizes the substances  
55 utilized in this study and Figure 2 presents their chemical structures. All the substances were  
56 laboratory grade (Sigma-Aldrich, UK) and the water was HPLC grade (Fisher Scientific, UK).  
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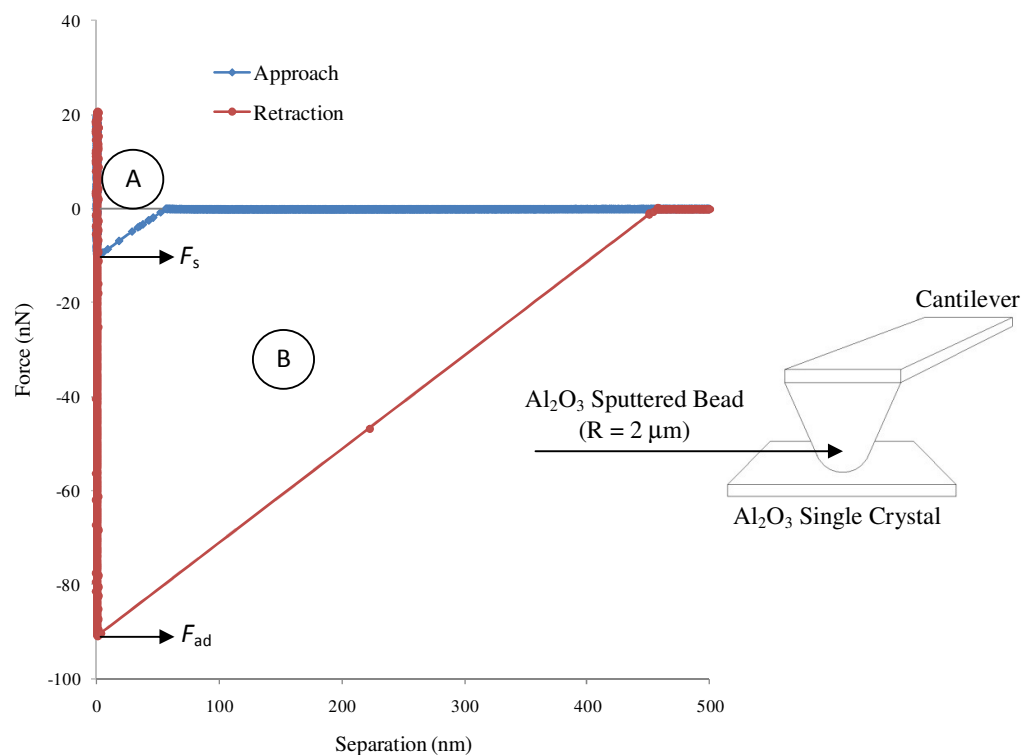


Figure 1. Schematic illustration of the sphere-on-flat geometry system (inset) and the typical experimental result for AFM force measurement of alumina in pure water: force (approach and retraction) versus separation between the cantilever and the single crystal. Parameters analysed: pull-off force ( $F_{ad}$ ) and adhesive energy ( $W \approx B$  = area formed by the hysteresis between the curves). Snap-on (jump-to-contact) force ( $F_s$ ) and area A are shown for comparative purposes.

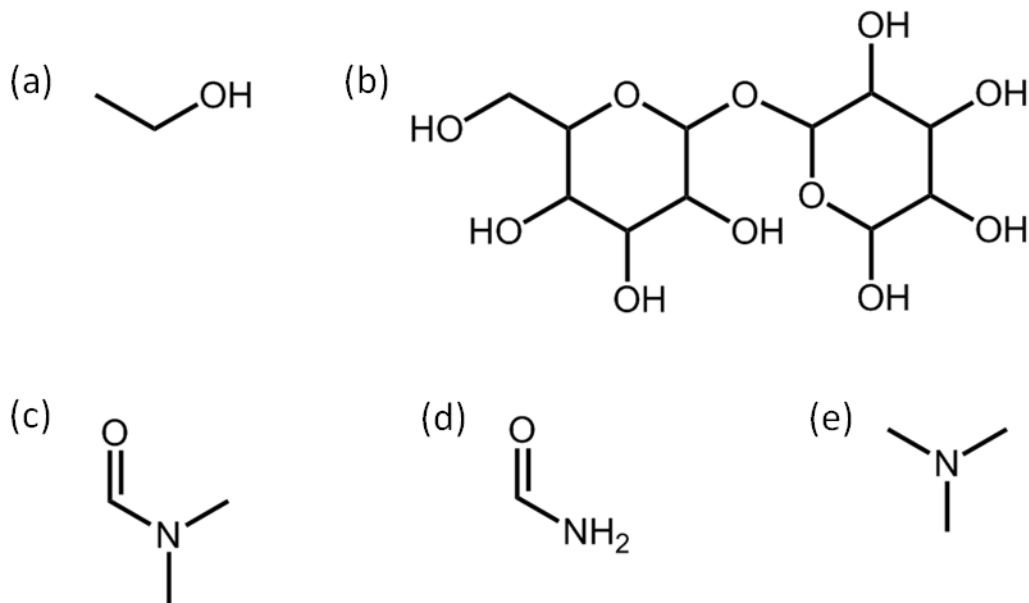


Figure 2. Chemical structures of substances used in this study: (a) ethanol (EtOH); (b) trehalose (THL); (c) dimethylformamide (DMF); (d) formamide (FA); and (e) trimethylamine (TMA).

Table 1. Physical-chemical aspects of substances used as aqueous solutions to probe adhesion at the nanoscale in between two alumina surfaces. All values relative to room temperature.

Substance	M <sub>w</sub> (g/mol)	Dielectric Constant	Surface Tension (mN/m)	Viscosity (mPa.s)	Refractive Index
Water (H <sub>2</sub> O)	18.01	80.0	73.0	1.00	1.33
Ethanol (≥99.5%, 200 proof, C <sub>2</sub> H <sub>6</sub> O)	46.07	24.3	22.1	1.20	1.36
Dimethylformamide (C <sub>3</sub> H <sub>7</sub> NO)	73.09	38.3	25.0	0.92	1.43
Formamide (CH <sub>3</sub> NO)	45.04	84.0	55.2	3.30	1.44
Trimethylamine (45wt%, C <sub>3</sub> H <sub>9</sub> N)	59.11	2.5	N/A	0.36	1.33
Trehalose dihydrate (C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ·2H <sub>2</sub> O)	378.33	N/A	N/A	N/A	N/A

## RESULTS AND DISCUSSION

Table 2. Pull-off force ( $F_{ad}$ ), snap-on force ( $F_s$ ), and adhesive energy ( $W$ ) acting at the contact in between the two alumina surfaces confining different aqueous solutions with varying molar fractions. Theoretical values – dielectric constant ( $\epsilon$ ), refractive index ( $n$ ), adhesion force ( $F_{th}$ ), and free energy ( $W_{th}$ ) – calculated according to the text.

Substance	Molar ratio of substance to water	$\epsilon$	$n$	$F_s$ (nN)	$F_{ad}$ (nN)	$F_{th}$ (nN)	$W$ (fJ)	$W_{th}$ (fJ)
Air	-	1.0	1.00	5.27 ± 0.83	107.76 ± 32.41	47	32.0	0.047
Water	0:1	80.0	1.33	6.71 ± 3.75	69.85 ± 31.76	15	10.7	0.015
EtOH <sub>1</sub>	1:500	79.5	1.33	0.22 ± 0.61	5.22 ± 3.10	15	12.1	0.015
EtOH <sub>2</sub>	1:50	75.3	1.33	0.84 ± 1.44	6.91 ± 4.01	15	0.35	0.015
EtOH <sub>3</sub>	1:4	49.7	1.34	0.43 ± 3.30	1.93 ± 1.05	14	0.09	0.014
EtOH <sub>4</sub>	1:1	33.7	1.35	0.27 ± 2.11	0.54 ± 0.33	13	0.04	0.013
EtOH <sub>5</sub>	4:1	26.9	1.36	0.10 ± 0.48	0.42 ± 0.20	13	0.03	0.013
EtOH <sub>6</sub>	1:0	24.3	1.36	0.19 ± 0.03	0.46 ± 0.17	13	0.03	0.013
DMF <sub>1</sub>	1:2000	79.9	1.33	10.85 ± 3.29	87.77 ± 18.28	15	15.0	0.015
DMF <sub>2</sub>	1:500	79.6	1.33	14.88 ± 3.42	101.90 ± 18.92	15	20.9	0.015
DMF <sub>3</sub>	1:50	75.9	1.34	14.09 ± 2.55	88.45 ± 5.43	14	16.2	0.014
DMF <sub>4</sub>	1:4	55.9	1.38	0.81 ± 0.43	4.73 ± 2.55	12	0.35	0.012
DMF <sub>5</sub>	1:2	49.4	1.40	0.53 ± 0.08	2.56 ± 0.45	10	0.32	0.010
DMF <sub>6</sub>	1:1	44.7	1.41	0.48 ± 0.13	1.66 ± 0.44	10	0.23	0.010
DMF <sub>7</sub>	2:1	41.7	1.42	0.38 ± 0.06	0.85 ± 0.27	9	0.16	0.009
DMF <sub>8</sub>	4:1	40.1	1.42	0.31 ± 0.07	0.57 ± 0.22	9	0.13	0.009
DMF <sub>9</sub>	1:0	38.3	1.43	0.10 ± 0.02	0.25 ± 0.08	9	0.03	0.009
FA <sub>1</sub>	1:500	80.0	1.33	1.63 ± 0.58	12.63 ± 4.16	15	1.21	0.015
FA <sub>2</sub>	1:50	80.2	1.33	1.69 ± 0.77	11.40 ± 3.63	15	1.11	0.015
FA <sub>3</sub>	1:4	81.4	1.37	0.48 ± 1.60	3.83 ± 1.69	12	0.34	0.012
FA <sub>4</sub>	1:1	82.7	1.41	0.54 ± 0.15	1.64 ± 0.69	10	0.21	0.010
FA <sub>5</sub>	4:1	83.6	1.43	0.90 ± 1.69	1.56 ± 0.78	9	0.20	0.009
FA <sub>6</sub>	1:0	84.0	1.44	0.60 ± 0.32	3.55 ± 1.44	8	0.86	0.008
TMA <sub>1</sub>	1:3000	79.8	1.33	2.15 ± 0.86	14.61 ± 4.94	15	0.98	0.015
TMA <sub>2</sub>	1:300	77.4	1.33	1.06 ± 0.55	4.78 ± 3.34	15	0.76	0.015
TMA <sub>3</sub>	1:30	59.0	1.33	0.86 ± 0.74	3.65 ± 2.09	15	0.40	0.015
THL <sub>1</sub>	1:3000	-	-	1.89 ± 0.69	13.43 ± 3.48	-	1.07	-
THL <sub>2</sub>	1:300	-	-	0.52 ± 0.67	8.93 ± 4.15	-	0.46	-
THL <sub>3</sub>	1:30	-	-	0.19 ± 0.22	10.16 ± 3.59	-	0.74	-



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3 The first measurement, performed under ambient conditions at room temperature, revealed a  
4 pull-off force  $F_{ad} = 107.76 \pm 32.41$  nN and adhesive energy  $W = 32.0$  fJ, as shown in Table 2.  
5 When submerged in water, the pull-off force dropped to  $69.85 \pm 31.76$  nN with adhesive energy  
6 of  $W = 10.7$  fJ. Capillary forces are usually important in force measurements taken in ambient  
7 air, but not in aqueous environments. Thus, we could infer the difference between the above  
8 pull-off forces to be the contribution of capillary forces to the adhesion of the alumina surfaces:  
9  $F_{cap} \approx 38$  nN. The theoretical value for the system under study was calculated previously as 27  
10 nN, which is very close to the experimental value, considering the latter does not carry the error  
11 propagation of the subtraction from which it arose. Contrarily, the comparison of experimental  
12 and theoretical force and energy results did not render good fittings. Firstly, let us compare the  
13 results of AFM force measurement performed under pure water: the adhesion force  $F_{ad} = 69.85$   
14  $\pm 31.76$  nN was considerably larger than the theoretical value, calculated as  $F_{th} = 15$  nN; so was  
15 the adhesion energy ( $W = 10.7$  fJ) relatively to the theoretical interaction free energy ( $W_{th} =$   
16  $0.015$  fJ), according to Table 2. One might find that the force accounting for the jump-to-contact  
17 of the surfaces,  $F_s = 6.71 \pm 3.75$  nN, was closer to the theoretical adhesion force, however the  
18 adhesion energy related to this force (equivalent to the area A in Figure 1, not shown in Table 2)  
19 was around one order of magnitude larger than the theoretical interaction free energy predicted  
20 for the system under study. Now, let us check what happened when we started adding the  
21 contaminants to the confined water.  
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26 Theoretically, a slight drop in the values of adhesion force and the interaction free energy was  
27 predicted after adding ethanol (EtOH) to water in comparison to the values of pure water.  
28 Nevertheless, as Table 2 shows, even with 1 EtOH molecule to 500 water molecules (Solution  
29 EtOH<sub>1</sub>) a large reduction in the pull-off force was noticed. Interestingly, the adhesive energy  
30 measured for such sample was nearly the same of that when pure water is the only substance in  
31 between the alumina surfaces. Adhesive energy of confined EtOH aqueous solutions started to  
32 decrease when EtOH concentration was increased significantly, from Solution EtOH<sub>2</sub> to pure  
33 EtOH (EtOH<sub>6</sub>), the latter presenting a pull-off force roughly three orders of magnitude lower  
34 than that of confined pure water. Pull-off force continually decreased with increasing EtOH to  
35 water molecular ratio in the aqueous solutions. From molecular dynamics (MD) simulations, it  
36 has been shown that there are 1.65 hydrogen bonds per EtOH molecule in liquid EtOH.<sup>22</sup> Dixit  
37 et al., using neutron scattering, found 3.6 hydrogen bonds per water molecule in pure water and,  
38 on average, around 2.3 hydrogen bonds per molecule in solution of 7 parts of methanol (MeOH)  
39 to 3 parts of water.<sup>23</sup> The authors concluded that, contrary to the speculation that water structure  
40 is either enhanced or destroyed in MeOH solution, the effect of MeOH on water was attributed  
41 to the relative strengths of MeOH-MeOH, water-MeOH, and water-water hydrogen bonds. This  
42 hypothesis was tested in this study by performing force measurements in aqueous solutions of  
43 formamide (FA) and dimethylformamide (DMF).  
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48 FA is the closest substance to water in terms of dielectric constant in this study; however, its  
49 refractive index is nearly the same that of DMF, what explains similar theoretical values for  
50 adhesion force and interaction free energy from both substances and points out the importance  
51 of van der Waals forces in a system where Coulombic charges are nearly absent. Having higher  
52 refractive index in comparison to pure water, both substances should comparatively drop the  
53 adhesion force as well as the free energy in between alumina surfaces with increasing their  
54 molar ratio to water. If we compare pull-off force and adhesive energy from confined pure water  
55 to DMF shown in Table 2 we conclude that both parameters are mostly reduced in the presence  
56 of the latter, except in solutions DMF<sub>1</sub> to DMF<sub>3</sub>. Interestingly, the pull-off force for solution  
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3 DMF<sub>2</sub> roughly equals that for measurements in air. Particularly, DMF differs in the ability to  
4 hydrogen bond when compared to water, the latter making four hydrogen bonds, as double  
5 acceptor and as double donor. According to our results, DMF could have been competing to  
6 accept water hydrogen bonds, for instance, when there is 1 DMF molecule to 4 other water  
7 molecules in aqueous solution, solution DMF<sub>4</sub>, or even more DMF to water molecules, like in  
8 solutions from DMF<sub>5</sub> to DMF<sub>8</sub>. The solutions DMF<sub>5</sub> to DMF<sub>8</sub> tend to sharply decrease the  
9 ability of confined water layers to adhere both alumina surfaces, what could be correlated to the  
10 strength of the formed hydrogen bonds. According to MD simulations from Lei et al., methyl  
11 hydrogen (H<sub>M</sub>) is a better donor than formyl hydrogen (H<sub>F</sub>) and the number of hydrogen bonds  
12 of formyl oxygen (O<sub>F</sub>) to methyl hydrogen is higher than the number of its hydrogen bonds to  
13 formyl hydrogen or to water hydrogen (H<sub>W</sub>); inherently, O<sub>F</sub> ··· H<sub>M</sub> is weaker than O<sub>F</sub> ··· H<sub>F</sub> or  
14 O<sub>F</sub> ··· H<sub>W</sub>.<sup>24</sup> Contrarily to DMF, all aqueous solutions of FA dropped both the pull-off force and  
15 the adhesive energy acting at the nanoscale in between two alumina surfaces when compared to  
16 pure water. Why such a discrepancy? The nature of hydrogen bonding in FA could be one  
17 reason. Theoretical calculations have shown that, even though hydrogen bonding is feasible at  
18 five active sites of FA, two electron-donor sites at oxygen and three electron-acceptor sites at N-  
19 H and C-H, primary solvation shell of FA may contain only four water molecules. Thus, water  
20 molecules interacting in the primary solvation shell are expected to be through hydrogen  
21 bonding with C=O and N-H moieties only.<sup>25</sup> Elola and Ladanyi reported that the average  
22 hydrogen bond distance between water and FA (1.85 Å) is smaller than that between two FA  
23 molecules (2.0 Å), suggesting that FA is able to form stronger hydrogen bonds with water than  
24 with another FA molecule.<sup>26</sup> It indicates that FA molecules are better hydrogen bond acceptors  
25 than donors in an aqueous environment. Their results also show longer values for lifetimes of  
26 hydrogen bonds among water molecules than between FA-FA and FA-water pairs, explained as  
27 a consequence of the water-water hydrogen bond being the strongest among the three types of  
28 hydrogen bonds that exist in FA-water mixtures. From Bakó et al., the mean number of  
29 hydrogen bonds per FA molecule is 3.21, while the number for water is 3.35.<sup>27</sup> Cordeiro et al.  
30 reported the formation of three hydrogen bonds between a FA molecule and its neighbouring  
31 waters, while two and one hydrogen bonds are formed in the case of methylformamide and  
32 DMF-water mixtures, respectively. As part of their conclusion, they observed that the strength  
33 of the amide-water hydrogen bond increases with decreasing the number of hydrogen bonds per  
34 amide.<sup>28</sup> This could be the reason for the different trends when comparing results of diluted  
35 solutions of DMF (DMF<sub>2</sub> and DMF<sub>3</sub>) to those of FA (FA<sub>1</sub> and FA<sub>2</sub>).

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42 Some highlights could be extrapolated from DMF and FA results: both substances show that it  
43 is possible, by slightly varying the solute concentration in the solution, to drastically alter the  
44 adhesive forces acting at the nanoscale between hydrophilic surfaces that confine a few water  
45 layers. This effect could be at the root of sea cucumbers ability of increasing the stiffness of  
46 their connective tissue by secreting macromolecules supposedly able to spoil the interactions  
47 mediated by water lying in between the collagen fibrils forming such tissue, under threatening  
48 conditions.<sup>13</sup> This effect could also be important to dictate the way proteins develop their  
49 function, since proteins resemble highly concentrated solutions where 20 to 50% of their crystal  
50 volume can be occupied by water molecules which, in turn, can make hydrogen bonds to their  
51 main chain through the C=O and N-H groups of the peptide unit or to the side chains through  
52 other polar groups. Bound water molecules were found to be linked to the peptide carbonyl  
53 groups in a proportion (42%) comparable to that found for the side chains (44%); in contrast, a  
54 low percentage (14%) of water molecules hydrated the peptide amino groups.<sup>29</sup> To check the  
55 effect of amino group on the confined water as an adhesive for alumina surfaces, we extended  
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our study using aqueous solutions of trimethylamine (TMA). Table 2 shows TMA continually drops the pull-off force as well as the adhesive energy up to a mole fraction of 1 TMA molecule to 30 water molecules; mole fraction was not increased beyond this point because ionization of TMA could affect the balance of charges in the system, and, thus, compromise the basis of our comparisons. Interestingly, spectroscopic characterization has shown that TMA-water hydrogen bond is around 1.82 Å long, among the shortest gas-phase hydrogen bonds yet measured. The drawback of TMA in terms of networking with water hydrogen bonds comes from the fact that its hydrogen bonds are linear or very nearly linear in nature, contrasting with the tetrahedral organization of water molecules.<sup>30</sup>

Since experiments insofar have also shown that viscosity, at least within the range we studied, does not seem to influence the results, one last parameter needed to be assessed: the influence of molecular size of substances added to speculate the role of confined water on the adhesion of two hydrophilic surfaces. Trehalose (THL) was chosen for such purpose and the results of these measurements are shown in Table 2. The presence of THL reduced the pull-off force and the adhesive energy between alumina surfaces, yet FA and TMA, which are smaller molecules than THL, had similar effects when present in dilute solution. On the other hand, the possibility remains that THL could have been squeezed out experimentally up to a point wherein it bridges both surfaces and hinders further confinement of water. This could be the reason for the nearly constant values of the measured parameters, regardless the THL concentration in the range of solutions herein investigated. Other studies have shown that addition of THL molecules to water leads to a significant increase in the population of water molecules that form none and one hydrogen bond with their neighbouring water molecules, at the expense of the water molecules population that form two, three or four hydrogen bonds.<sup>31</sup>

So, the ability of contaminants to distort the way water organizes itself as well as the number of their hydrogen bonds with water seem to be the most plausible factors affecting the power of water in giving adhesion of the alumina surfaces of this study. In fact, water owes such feature to the tetrahedral coordination enabled by its hydrogen bonds. Hydrogen bonds are reasonably directional and strongly attractive, so that they can be very strong at short-range. This non-DLVO force is likely to determine the adhesion between the alumina surfaces at the contact, what is confirmed in the present study by the deviation of the experimental results in relation to those theoretical ones. Such deviation, seen throughout Table 2, highlights the limitation of the predicted theoretical adhesion, which, in turn, is due to the assumption of both the surfaces and the solvent medium as continuums. By doing this, the theory leaves no room for the molecular effects as sensitive as those we showed by the influence of contaminants on the water-water interactions. Nevertheless, such deviation should not represent a breakdown in the DLVO interactions.<sup>3</sup> In other words, we would expect adhesion force to assume an asymptotic value corresponding to the contribution of electrostatic and van der Waals forces when the hydrogen bonding network of the confined water was disturbed, but, somehow, it was not observed. Presently, we cannot exclude the effect of the solutes preferentially replacing water from the interface with both alumina surfaces, and its influence on the overall adhesion. Future molecular dynamics simulations could clarify whether it is relevant or not, however, the results of the dilute solutions of dimethylformamide suggest that it is not.

## CONCLUSIONS

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3 It has been shown that in the presence of water, two hydrophilic alumina surfaces are attractive  
4 to each other and experience an adhesion that can be modified either by the capillary forces or  
5 by subtle modifications in the way water organizes itself. Differences either in the ability to  
6 form hydrogen bonds or in the number of hydrogen bonds from donors and acceptors of the  
7 solutes to water proved to be the most important parameter in terms of enhancing or (mostly)  
8 spoiling the adhesion of the surfaces through the confined water layers. Presently, we cannot  
9 exclude the effect of solutes preferentially replacing water from the interface with both surfaces,  
10 and its influence on the overall adhesion. Future molecular dynamics simulations could clarify  
11 whether it is relevant or not, however, the results of the dilute solutions of dimethylformamide  
12 suggest that it is not. Thus, it is hoped that this investigation of the role of confined water on the  
13 adhesion of surfaces could shed some light into disciplines ranging from materials science to  
14 biology and reinforce the idea that water cannot always be treated as a continuum defined solely  
15 in terms of its bulk properties.  
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