

Investigations of the Force–Distance Behavior in Polar Liquids

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Scanning force microscopy (force–distance curves) is employed to study the interaction of two SiO_x surfaces in a homologous series of hydrogen-bonded liquids. The force–distance behavior and adhesion, determined by solvation effects as well as van der Waals and electrostatic forces, vary systematically with the structure of the liquid molecule. A model is proposed which relates the molecular arrangement in the confining geometry of the tip and the underlying surface to the number of hydroxyl groups of the solvents (hydrogen-bonded networks). For a quantitative evaluation, the spring constant is calculated from the geometric parameters and the eigenfrequencies of the cantilever.

Introduction

Force measurement performed by a scanning force microscope (SFM) have been established, alongside the surface forces apparatus (SFA), as a valuable tool for investigations on the molecular interactions of surfaces. The advantages of the SFM are the flexibility in the choice of the surface material (not limited to mica), the possibility of imaging the properties of the surface around the contact point by scanning, as well as the considerably reduced experimental effort. van der Waals forces (attractive or repulsive), first determined by SFA, have been verified by SFM for a variety of surface combinations, (see, for example, refs 1 and 2), and the Hamaker constants have been estimated.^{3,4} The solvation in liquids, especially the hydrophilic and hydrophobic interaction, has been investigated.^{5–7} Most studies concentrate on the behavior before contact, as a number of problems make the interpretation of adhesion data more complex,⁸ such as the influence of the surface roughness, vertical sliding of the tip in contact with the surface causing torsions, higher bending modes,⁹ limited detection of the cantilever deflection on commercial SFMs,^{10,11} and undefined size of the contact area. Nevertheless, the adhesion has been studied in quite a number of investigations.^{12–15} A statistical analysis has been used by Hoh et al.¹⁶ and by Williams et al.^{17,18} in hydrogen-bonding systems. However, the force of the single hydrogen-bond determined by both groups differs by a factor of 15.

To reduce the influence of the size of the surface area, in many cases only one tip was used for a whole series of measurements.¹⁹ The limiting factor for a quantitative analysis of the force measurements is the cantilever spring constant. A simple method for the determination of the spring constant will be introduced in the Experimental Section.

Much interest is being paid currently to the influence of a geometric confinement on the properties of molecular systems. The dynamics of low-molecular-weight glassforming liquids in nanoporous sol–gel-glasses was studied via broadband dielectric spectroscopy.^{20,21} In hydrogen-bond liquids, only one relaxation process is observed, which is strongly broadened on the low-frequency wing, compared to the bulk material. An analysis of

the relaxation strength shows that a number of molecules in the pores no longer relax in the given time window. These results may be explained by a model of a layer of molecules firmly attached to and immobilized by the pore walls, and an intermediate layer adapting the dynamics to the bulklike molecules in the pore center. Force–distance measurements with analogous surfaces in a variety of glassforming polar or nonpolar liquids confirm these results and provide further information.

Experimental Section

For all measurements, a NanoScope IIIa/D3000 SFM (digital instruments, Santa Barbara, CA) was used. Force curves were obtained with single-beam Si cantilever (S3G2T1-3L450-B, Nanosensors) and glass slides (B270 Superwrite, Gebr. Rettberg, Germany). As silicon surfaces in air are always covered by an amorphous oxide layer, the setup may be considered as symmetrical: solvophilic SiO_x surfaces with a density of OH groups of 4–5 /nm², half of which are isolated and half vicinally bonded.²² For surrounding medium, several low-molecular-weight hydrogen-bond forming liquids were chosen (cf. Table 1). The liquids were chosen according to structural aspects. In propanetriol, hydrodynamic effects due to the high viscosity (Table 1) had an obvious influence on the force curves for cantilever velocities >40 nm/s, all measurements were therefore performed with 8 nm/s. Before measuring the glass slides, they were exposed to commercial glass cleaning solution (Küvettol, neoLab) at 40 °C for about 15 min in an ultrasonic bath. Then they were repeatedly rinsed with deionized water and thoroughly dried in a N₂-stream (5N). The cantilevers were washed in pure ethanol (Merck) and dried in the N₂-stream.

For every liquid, five sample spots were chosen on which the roughness was small (root-mean-square roughness <3 nm on 1 μm²); for each one, the cantilever deflection was calibrated vs the scanner position in the contact area, and between 20 and 60 force curves were determined. The SFM height and deflection signals were calibrated according to ref 23. The interactions during bringing the surfaces closer together (inward run) and pulling them apart (outward run) were considered. The raw data (cantilever deflection vs scanner position) will be called “force curves”, whereas “force–distance curves” are rescaled to show the force vs the tip–sample distance. The SFM software limits the resolution to 1024 data on every approach, e.g., 1024 data points on 2 × 100 nm scanner movement.

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TABLE 1: List of the Liquids Used (n : refractive index, η : viscosity)

| liquid | Σ -formula | n_D (20 °C) | density | η (20 °C) | vapor pressure |
|-----------------|-------------------|---------------|-------------------------|----------------|----------------|
| 2-butanol | C_4H_9OH | 1.3970 | 0.808 g/cm ³ | 4.21 mPas | 17.3 hPa |
| 1,2-propanediol | $C_3H_6(OH)_2$ | 1.4320 | 1.036 g/cm ³ | 45 mPas | 12 hPa (80 °C) |
| propanetriol | $C_3H_5(OH)_3$ | 1.474 | 1.261 g/cm ³ | 1400 mPas | |

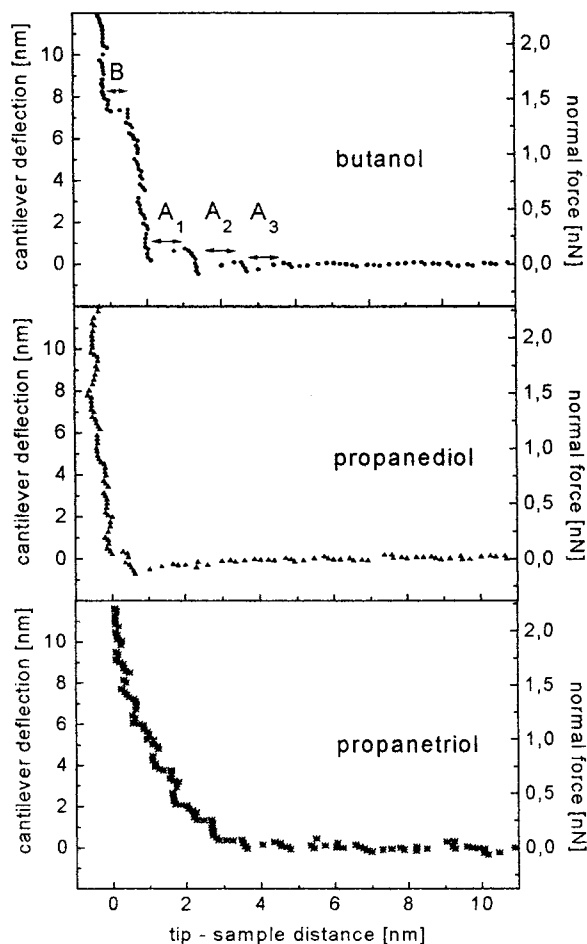


Figure 1. Force–distance curves of inward runs in butanol, propanediol, propanetriol. All measurements performed with a single cantilever, resolution 0.2 nm/pixel \leftrightarrow 2×100 nm scanner movement, $v = 8$ nm/s. The overall interaction behavior is DLVO or van der Waals type for butanol and propanediol, repulsive behavior in propanetriol. Besides, a fine structure due to the molecular characteristics of the three alcohols becomes visible: In butanol, oscillations (marked as A_i) are seen, the force increases with decreasing distance. In contact (slope $\rightarrow \infty$) a further jump (B) occurs. In propanediol, a single jump may be observed. Noise in the baseline, determined for 20 nm scanner movement: ± 0.1 nm for butanol and propanediol, ± 0.2 nm for propanetriol.

The error due to spring constant and contact area of the tip was reduced by measuring all curves with a single tip. The spring constant of the cantilevers was determined with a method combining the geometric parameters (measured with a scanning electron microscope) and the eigenfrequencies of the cantilever (determined by sampling the resonance frequencies during driven oscillation, second through sixth mode). As the spring constant determined in this way is linear in the geometric dimensions, the total error is 4% compared to more than 10% error for the methods described in refs 24–31. The spring constant determined for the tip used in the present investigations was (0.19 ± 0.08) N/m.

Results

Figure 1 shows force–distance curves of approaching surfaces for the three polar liquids 2-butanol, 1,2–propanediol, and

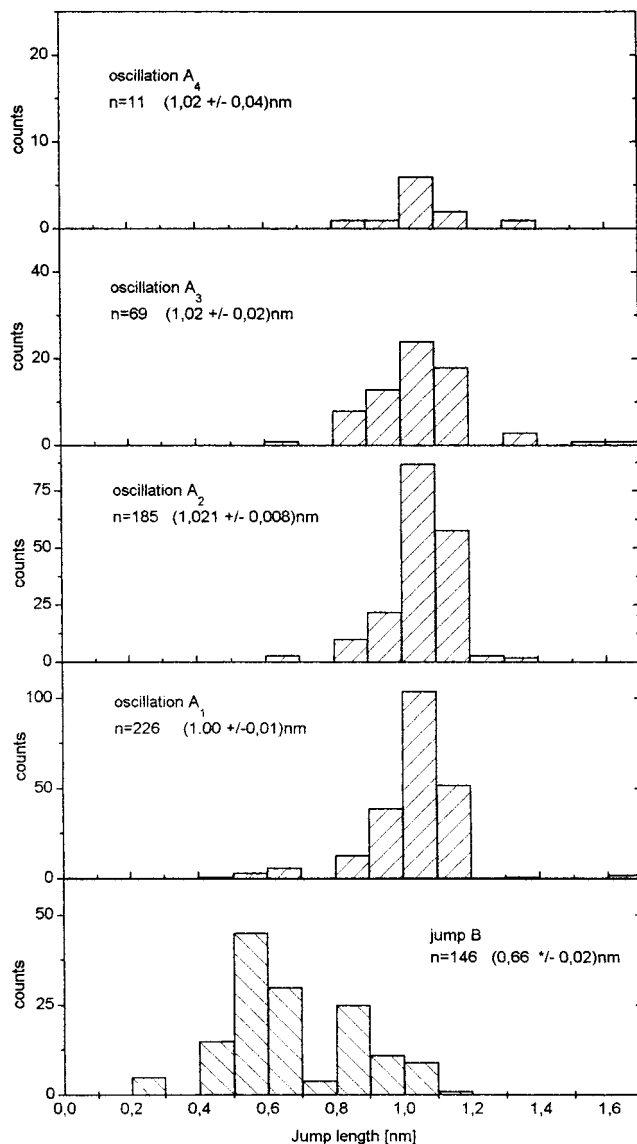


Figure 2. Histograms of the jump lengths in butanol. A total of 244 force–distance curves were analyzed. The A_i indicate force oscillations during approach, B an additional force jump in the immediate vicinity of the surface, cf. Figure 1. The mean jump lengths and standard deviation are given as well as the number n of curves in which the corresponding jump occurred in a quantifiable manner.

propanetriol. Up to a distance of 6 nm from the contact point, a substance–dependent fine structure of the interaction behavior is seen, in the butanol medium, for tip–surface distances smaller than 5 nm, up to four oscillations (marked as A_i in Figure 1) were observed. Besides, one or occasionally two additional jumps (marked as B in Figure 1) are seen in the part of the force–distance curve which corresponds to contact of tip and surface (slope approaches infinity). The jump distance for jumps of type A and B is determined in 244 force curves, 226 of which show at least one jump of type A, and 146 show a jump of type B. The histograms are shown in Figure 2. The length scale of all four oscillations A_i is 1.01 nm, only the variance decreases with the distance. Their amplitude increases from 0.04 nN (resolution limit) up to 0.4 nN. The jumps of type B range

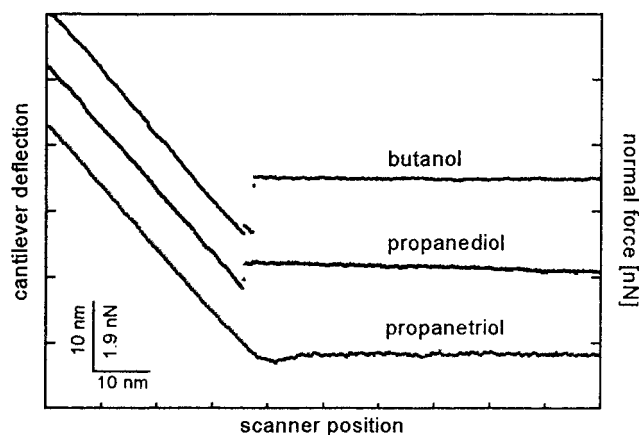


Figure 3. Typical force curves of outward runs (adhesion) in different polar liquids (arbitrary y-offset). Resolution 0.2 nm/pixel $\leftrightarrow 2 \times 100$ nm scanner movement, $v = 8$ nm/s, all measurements performed with a single cantilever. In butanol and propanediol, a pronounced adhesion is visible, in contrast to the repulsive force between two SiO_x surfaces in propanetriol.

between 0.3 and 1.2 nm, with a wide variance. The number of oscillations that can be measured quantitatively as well as the occurrence of jumps of type B are reproducible for each measuring spot, so they seem to be related to the local surface geometry. The underlying behavior is attractive, as may be seen when no or few oscillations occur.

For the force–distance curves obtained in propanediol, a single jump of either type is occasionally observed, e.g., 0.8 nm, 0.2 nN, as in Figure 1, but without the oscillatory force behavior A seen in butanol. Close to the contact point, the noise is slightly increased compared to that observed in butanol, and some drift occurs in the force–distance curve. If no such jump is seen, the behavior is attractive. In propanetriol, no jumps were observed at all. The repulsive force between the tip and the surface is superposed by some noise (RMS 0.2 nm compared to 0.1 nm in propanediol and butanol); however, Fourier transform analysis shows no periodicity.

In Figure 3, typical force curves of the outward run are shown for all three liquids. For butanol and propanediol, a pronounced adhesion behavior is seen, while in propanetriol no adhesion is observed at all. In butanol the adhesion strength varies significantly, values between 0.2 and 7 nN were found, with an average of 0.9 nN and standard deviation of 0.6 nN (Figure 4). The jump from contact repeatedly occurs via intermediate positions. Often these jumps are observed while the tip is still in contact, analogous to the behavior seen in the inward run. The adhesion behavior (strength, jumps) is again strongly correlated with the position on the glass substrate and, therefore, with the local geometry of the contact area. For a single measuring spot, the force curves are reproducible. The adhesion strength in propanediol is significantly smaller (Figure 3), with a mean of 0.5 nN and a standard deviation of 0.3 nN.

Discussion

The dependency of the interaction of SiO_x surfaces in the present series of hydrogen–bond liquids, namely butanol, propanediol, propanetriol, can be explained by the molecular character of each liquid given mainly by the number of hydroxyl groups of the molecule, as the length of the molecules is comparable. A butanol molecule with a single OH group can form only one hydrogen bond, so that the molecules form complexes of two molecules with the polar moiety in the center and a solvophobic outside (Figure 5). In the confined geometry

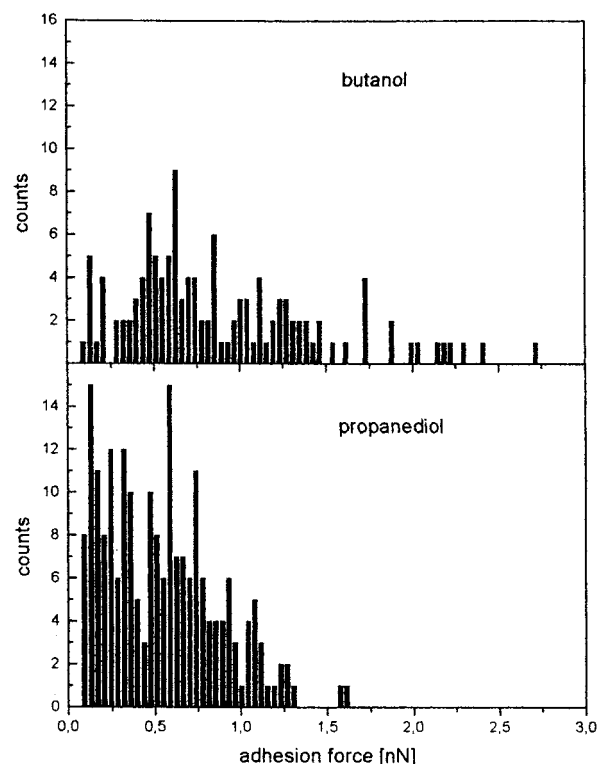


Figure 4. Histograms of the adhesion strength in butanol and propanediol. If several jumps occurred in one force curve, only the last jump is considered. The mean values are (0.9 ± 0.6) nN in butanol, respectively, (0.5 ± 0.3) nN in propanediol.

of the gap formed by the glass slide and the approaching tip, butanol displays a solvation behavior indicating that layers of these molecular complexes are formed, the periodicity of the oscillatory force (jumps A_i , 1.01 nm) correlates well to the dimensions of the said complexes (between 0.8 and 1.1 nm, depending on the conformation). This solvation behavior, first described for SFA experiments,³² is due to a molecular arrangement as a result of the confining geometry. If an integer number of layers fits in the gap between two planar approaching surfaces, the repulsive force is comparatively high. As the loading force increases with a narrowing gap, the system becomes unstable until the width of the gap corresponds again to an integer number of layers. The fewer the number of layers is, the better the ordering and the stronger the force needed for the break down. According to Israelachvili,³⁵ an exponential increase of the oscillation amplitudes is expected. The last solvation jump B (0.6 nm) occurring when the tip is already exerting a force, corresponds to the removal of surface–bound molecules. The adhesion strength relates to the area where all alcohol molecules are removed and the SiO_x surfaces touch one another. The variance of the adhesion indicates that this area is different on every approach (Figure 4).

In propanediol, each molecule can form two hydrogen bonds, so that an interconnected molecular system is formed. The liquid is pushed out of the contact area continuously, so no oscillations occur. Only the molecules at the surface form a well-defined layer, which may occasionally cause a single jump of type A. Again, the adhesion varies, indicating that even when in contact, part of the surfaces remain covered by alcohol molecules. Due to the second hydroxyl group they are more strongly bound. This has two consequences: A solvation jump (type B), which is seen only when a significant part of the layer is pushed out

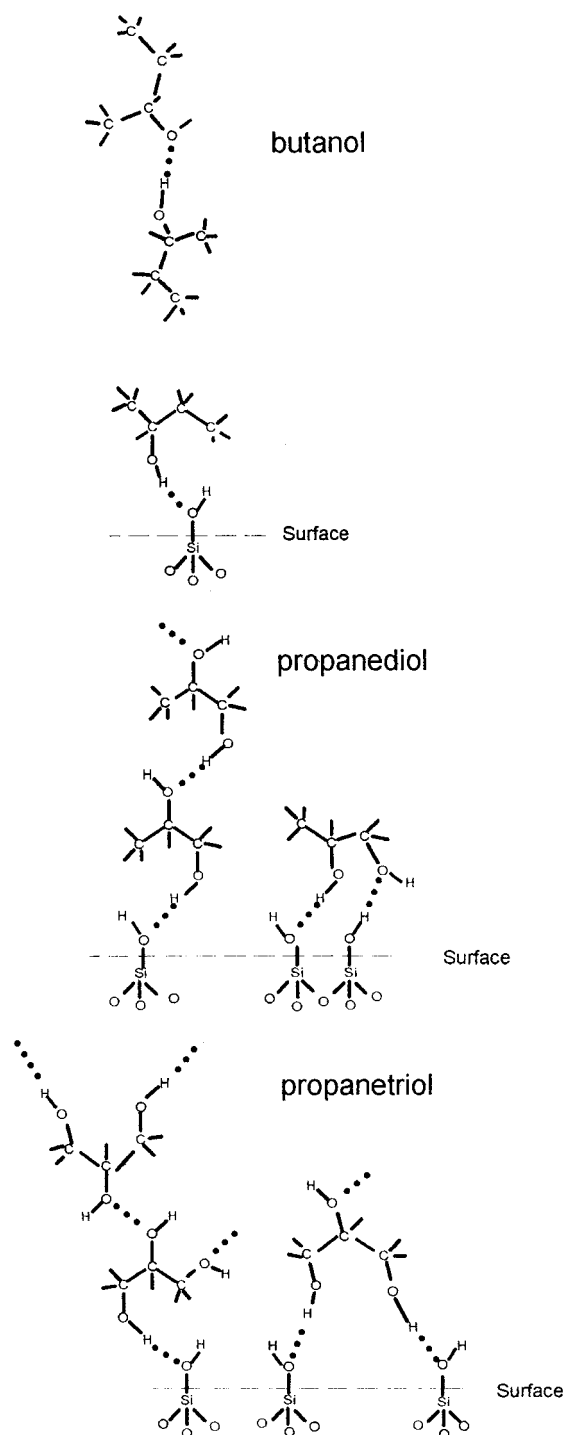


Figure 5. Cartoons of hydrogen-bonded complexes of (a) 2-butanol, (b) 1,2-propanediol, and (c) propanetriol molecules.

of the gap at once, occurs only occasionally and the mean adhesion strength (SiO_x contact area) is decreased compared to butanol.

Propanetriol has three hydroxyl groups and therefore a distinct network-forming character (hydrogen bond), a layer packing of the molecules is no longer feasible. The repulsive interaction and lack of adhesion indicate that a layer of firmly bound liquid molecules keeps the two surfaces apart. A similar interaction behavior would be seen if the high viscosity of the liquid impeded the movement of the cantilever; however, the velocity of the cantilever was set so that at some distance from the contact point no hydrodynamical influence on the cantilever was seen (force–distance curve parallel to distance axis).

The studies of the system glass/2-butanol/Si-tip presented in this paper are completely consistent with those of the friction behavior of O'Shea et al.³³ in the system mica/*n*-dodecanol/ Si_3N_4 tip. Both systems are comparable in the chemical constitution of the surfaces (Williams et al.¹⁸ maintain a SiO_x surface on Si_3N_4). Close to contact, oscillations with increasing amplitude were observed in the force–distance curve, the period relates to double layers. O'Shea et al. could show via friction force measurements performed parallel to the force measurements that the last of the jumps occurring when already in contact, which corresponded to a force difference half the size of all previous jumps, pertains to the last layer of molecules, singly bound to the surface. The force–distance behavior beyond the superimposed short-range solvation seems to be comparable as well, with a weak medium range attraction and stronger short-range repulsive behavior. In other measurements that O'Shea et al. performed on chemically inert graphite in a OMCTS (octamethylcyclotetrasiloxane) liquid medium, the underlying interaction is purely attractive.³⁴ In an *n*-dodecanol medium, the oscillation period depends on the substrate: on mica it relates to an edge-on orientation,³³ while on graphite a side-on orientation of the molecule (solvophobic alkyl chain) may be deduced.³⁴ Here, the superimposed interaction is purely repulsive.

The adhesion behavior of butanol is similar, both with respect to strength and variance (values between 0.2 and 7 nN) to that of *n*-dodecanol reported in,³⁴ which varies between 1 and 100 nN; here, smaller solvation-like jumps before the final separation of the surfaces were noticed. Parallel measurements determined a simultaneous decrease of the friction force, permitting an interpretation of the jumps as liquid flowing into the gap in the contact area.

Conclusion

In SFM force–distance investigations of two SiO_x surfaces in 2-butanol, 1,2-propanediol, and propanetriol, both the force–distance behavior and the adhesion vary systematically. This dependence on the molecular structure of the liquids forming the surrounding medium is seen on one hand in the degree to which a layer of surface-bound molecules keeps the two SiO_x surfaces apart and “passivates” the electrostatic or van der Waals attraction as well as on the other hand in solvation behavior, which points toward a molecular arrangement of the liquid molecules in the confining geometry. In butanol, an attractive behavior on the inward run and pronounced adhesion indicate only weak bonding of the liquid to the surface via the single hydrogen bond; in propanediol, the adhesion is smaller, corresponding to smaller surface area actually coming into contact, whereas in propanetriol, the repulsive behavior is due to a firmly bound surface layer. More information may be deduced from the solvation behavior, which is rarely seen in SFM measurements, as an extremely high resolution is necessary. The results are explained by a model proposed for the molecular arrangement due to the confining geometry: Butanol with only one hydroxyl group has a quasi-amphiphilic character and tends to form layers in the gap. With a rising number of hydroxyl groups per molecule, the influence of the hydrogen-bond network increases and impedes the formation of surface-induced ordering.

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