

Hydroxide Ion Adsorption on Self-Assembled Monolayers

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Abstract: It is argued, on the basis of density functional calculations, that a self-assembled monolayer of oligo(ethylene glycol) or *n*-alkanes in contact with water will preferentially adsorb hydroxyl ions (either from autoionization of water or added to the solution) on both methoxy- and hydroxide-terminated endgroups, thus charging the surface region of the SAM negatively with an estimated charge density of about 1 $\mu\text{C}/\text{cm}^2$ in agreement with recent experiments. The negative charging can explain long-ranged forces between opposing SAM surfaces. On dense SAMs, hydroxyl ions are highly mobile. Hydronium ions can adsorb by penetration into the SAM provided there is enough lateral space for their encapsulation. The important role of hydration is demonstrated by calculating the excess binding energy of adsorption using a Born–Haber cycle.

1. Introduction

One of the overriding issues in the current study of oligo(ethylene glycol) (OEG)-terminated self-assembled monolayers (SAMs) is the origin of the long-ranged forces (>10 nm) between opposing SAM-covered surfaces immersed in water as was measured with the atomic force microscope or in the surface-force apparatus. A remarkable and important feature of these organic monolayers is the strong dependence of their properties on their packing density, which can be manipulated by the substrate on which the films are formed.¹ Au-supported methoxy tri(ethylene glycol)-terminated undecanethiolate SAMs (EG3-OMe), on which the molecules have an average areal density of 4.6 nm^{-2} , repel each other in aqueous electrolyte solutions. These surfaces are of great interest in the field of biomaterials because of a pronounced resistance to blood-plasma protein adsorption. By contrast, SAMs on Ag with an average areal density of 5.3 nm^{-2} show attraction and adsorb proteins from solution.^{2,3} The repulsive interaction found for the Au-supported SAMs depends on the electrolyte concentration and scales with the Debye screening length.^{2,4} This is a surprising finding, because ethylene glycol is a nonionic surfactant, and it is not clear what the origin of the electrostatic repulsion is. The adsorption or incorporation of ions into the film is an unlikely reason, because systematic measurements using different salts (Hofmeister series) showed the same screening behavior in solution, independent of the kind of monovalent ions used.⁵ Further experiments by Dicke and Hähner demonstrated that

the repulsive interaction at constant ion concentration also depends on the pH of the solution and diminishes around pH 4.⁶ This rules out effects by electrolyte ions and leaves preferential adsorption of water ions as a primary explanation of surface charging on hydrophobic surfaces.^{7,8} The suggestion by Dicke and Hähner and Pertsin et al.^{6,9} that hydroxide ions either preferentially adsorb on or are incorporated into the Au-supported SAM was confirmed in streaming potential experiments,¹⁰ in which a negative ζ potential at neutral pH (-120 mV) decreasing to zero at pH 4.4 and then becoming positive at even lower pH values was observed. Concentration-dependent measurements with different electrolytes, including HCl, support the hypothesis that hydroxide ions are responsible for the negative surface charge. Pertsin et al.⁹ suggested a mechanism in which the interfacial negative charge originates from an asymmetric adsorption of the products of water autodissociation, viz. from the preferential adsorption of hydroxide, OH^- , over hydronium, H_3O^+ , as it occurs in thin aqueous foam films stabilized by OEG *n*-alkyl surfactants.¹¹ It is important to note, however, that negative ζ potentials have been observed against hydrophobic polymers as well as methyl- and OH-terminated SAMs.^{12–14} Curiously, however, repulsive surface forces between these SAMs immersed in water have not been observed, and no special resistance to protein adsorption is noted for these surfaces.

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(1) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B* **1998**, *102*, 426.
(2) Feldman, K.; Hähner, G.; Spencer, N. D.; Harder, P.; Grunze, M. *J. Am. Chem. Soc.* **1999**, *121*, 10134.
(3) Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 10714.
(4) Dicke, C.; Feldman, K.; Eck, W.; Herrwerth, S.; Hähner, G. *Polym. Prepr.* **2000**, *41*, 1444.
(5) Dicke, C.; Hähner, G. *J. Phys. Chem. B* **2002**, *106*, 4450.

(6) Dicke, C.; Hähner, G. *J. Am. Chem. Soc.* **2002**, *124*, 12619.
(7) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Veleev, O. D.; Petsev, D. N.; Ivanov, I. B.; Brownkar, R. P. *Langmuir* **1996**, *12*, 2045.
(8) Werner, C.; Körber, H.; Zimmerman, R.; Dukhin, S.; Jacobasch, H.-J. *J. Colloid Interface Sci.* **1998**, *208*, 329.
(9) Pertsin, A. J.; Hayashi, T.; Grunze, M. *J. Phys. Chem. B* **2002**, *106*, 12274.
(10) Chan, Y. H. M.; Schweiss, R.; Werner, C.; Grunze, M. *Langmuir*, submitted.
(11) Karraker, K. A.; Radke, C. J. *Adv. Colloid Interface Sci.* **2002**, *96*, 231.
(12) Schweiss, R.; Welzel, P.; Werner, C.; Knoll, W. *Langmuir* **2001**, *17*, 4304.
(13) Werner, C.; Zimmerman, R.; Kratzmüller, T. *Colloids Surf., A* **2001**, *192*, 205.
(14) Zimmerman, R.; Dukhin, S.; Werner, C. *J. Phys. Chem. B* **2001**, *105*, 8544.

Water interaction with oligomers of ethylene glycol (diglyme) has been studied by ab initio methods by us and Smith et al.^{15,16} Here, we briefly review our previous work on the structure and energetics of short OEG molecules, (EG)_n with $n = 1, 2, 3, 4$, and their interaction with neutral water molecules.¹⁵ On the basis of density functional calculations, we showed that, in vacuo, their most stable conformer was helical and that the incorporation of gauche defects is energetically very costly because they bring the oxygen atoms on subsequent EG subunits closer together, thus enhancing their Coulomb repulsion. However, in contact with water, the conformers with gauche defects, in particular those with a $g^+g^-g^+$ sequence, are energetically most favored because they can be deformed to such a degree that from four to five hydrogen bonds can be established between one or two water molecules and the three subsequent EG subunits forming hydrogen-bonded bridge structures.

As far as the interaction of water on the end groups of OEG is concerned, adsorption of water on a methyl group seems not possible by hydrogen interactions only (i.e., neglecting small contributions from dispersion forces); our estimate for this binding energy is less than 5 meV/molecule, which is at the level of accuracy of the method. On the other hand, adsorption of water on hydroxy-terminated OEG is quite strong. For a single water molecule, the binding energy is 0.25 eV. Both estimates are also true for methoxy- or hydroxy-terminated *n*-alkane chains.

In this paper, we will show, on the basis of density functional calculations, that a self-assembled monolayer of oligo(ethylene glycol) or *n*-alkanes in contact with water will show preferential adsorption of hydroxyl ions on both the methoxy- and the hydroxide-terminated endgroups. This is already the case when autoionization of neutral water is the only source of ions but obviously even more so when hydroxyl ions are added to the system (for instance, by adding potassium hydroxide to the solution).

The paper is structured as follows: In the next section, we specify our choice of ab initio methods, the density functional theory with gradient corrected exchange/correlation potentials and a large basis set. The first application is to the hydration of hydroxyl and hydronium ions. The remaining calculations are done for oligo(ethylene glycol) and for *n*-alkanes interacting with water and its ions. We then demonstrate that our method reproduces the known experimental fact that single OEG molecules in water will encapsulate hydronium ions. Next, we investigate the geometry and energetics of the adsorption and absorption of hydroxide ions. A careful analysis based on a Born–Haber cycle shows that hydrated OH⁻ ions will adsorb on a SAM preferentially between two and three terminal methyl groups (bridge and hollow sites in the following) of methyl-terminated polymers such as OEG and *n*-alkane, leading to a negative charge accumulation of about 1 μC/cm², in good agreement with the electrokinetic measurements.¹⁰ In the last section, we discuss the implications for long-ranged electrostatic forces, pointing out the important role of charge mobility for the latter.

A brief comment on terminology follows: the term adsorption refers to binding of molecules on a surface. If the latter is the

termination of an inorganic, more or less impenetrable, solid, adsorption is a self-evident concept. This is, however, not so straightforward with soft matter which has deformable and penetrable surfaces. In such situations, adsorption on the surface and absorption in the surface region are interchangeable and overlapping concepts.

2. Ab Initio Calculations

2.1. Preliminaries. Our calculations of the structure and energetics of the adsorption of water and its ions on OEG are done for small clusters as we have done in our previous work on water adsorption on OEG,¹⁵ and as most ab initio approaches to water quantum chemistry also employ. Some care must then be taken to extrapolate the results to the bulk solution. Yet we will see that increasing the number of water molecules, and to a lesser extent of OEG molecules, will produce a convincing trend toward bulk behavior. Our motivation for a cluster approach is the fact that it allows us to use sophisticated and accurate ab initio methods. We will base our calculations on the density functional theory as implemented in the Gaussian 98 suite of programs.¹⁷ Because the success of the density functional theory hinges to a large part on the proper choice of the exchange/correlation potential, we have, in our previous work, tested a number of choices and compared the results with MP2 calculations. For the following calculations, we have chosen the option BP86/6-311++G** in Gaussian 98 for which, as one justification, the same stability series for the various conformers of (EG)₃ was obtained as with the best MP2 calculations.

As for CounterPoisson corrections to account for the basis set superposition error (BSSE), we recall that without (with) BSSE corrections binding energies of clusters are over- (under-) estimated and the algebraic mean is a good approximation,^{18,19} which we will also adopt in this paper. Once a method and a basis set have been chosen (with some reasonable arguments as outlined above), relative energies of various conformers of the same system are usually obtained with much higher accuracy.²⁰ For future reference, we define the binding or association energy of a complex formed in a reaction



as the difference in the total electronic energies of the reactants and products, that is

$$E_B = E_{\text{total}}[A] + E_{\text{total}}[B] - E_{\text{total}}[AB] \quad (2)$$

(15) Wang, R. L. C.; Kreuzer, H. J.; Grunze, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3613–3622.

(16) Smith, G. D.; Jaffee, R. L.; Yoon, D. Y. *J. Phys. Chem.* **1993**, *97*, 12752–12759.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(18) Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1996**, *100*, 2993–2997.

(19) Xantheas, S. S.; Burnham, C. J.; Harrison, R. J. *J. Chem. Phys.* **2002**, *116*, 1493–1499.

(20) Smith, A.; Vincent, M. A.; Hillier, I. H. *J. Phys. Chem. A* **1999**, *103*, 1132–1139.

The adsorption of hydroxide or hydronium ions on OEG or *n*-alkane molecules or SAMs from bulk water is accompanied by a partial breaking of their hydration shells. We must therefore first establish the energetics of (i) the charge transfer process in autoionization itself and (ii) the subsequent formation of the hydration shells around isolated ions in water. Much theoretical work has been published on this problem in the past decade, mostly at the MP2 level or using the density functional theory for small clusters with typically less than 10 water molecules. Hydration free energies (Gibbs free energy changes) of the proton have been calculated,^{22,23} as well as total energies, association enthalpies, and vibrational spectra of hydroxide–water clusters.^{24–27} A major advance came with the ab initio molecular dynamics calculations by Trout and Parinello^{28,29} of the p*K* value of the equilibrium constant of the autodissociation of water, which yielded a free energy difference of 0.8 eV, very close to the experimental value of 0.87 eV. Shortly thereafter, an actual kinetic pathway was found which indicated that the process of autoionization is completed once the two ions are separated by three or more water molecules.²¹ What makes any calculations of the autoionization of water so difficult are, not surprisingly, the effects of the long-range electric field of the ions on the surrounding water dipoles. Autoionization is a sequence of steps in which the proton transfer from one molecule to a neighbor must be accompanied by the simultaneous formation of a hydration shell around the nascent ions. It is the long-ranged electric fields that orient surrounding water molecules in this process.

Unfortunately, the above calculations do not provide all of the cluster energies that we need within one calculational scheme; that is, either the method or the basis sets are different from what we chose on the basis of our calculations for the interaction of water with OEG. It is very important to do all of the calculations within one framework, that is, for water clusters, hydration of hydroxide and hydronium ions, and their respective interaction with OEG. We have therefore repeated the cluster calculations for the hydration of the ions with the basis set and the choice of exchange/correlation potential given above. We find that the autoionization of water in the gas phase



requires an ionization energy of 9.65 eV. Almost all of this energy is then released again in the subsequent hydration of the ions. These hydration energies are compiled in Table 1, where we also give the available values from the literature. The differences are within the confidence levels of the calculational methods chosen and should not affect the general trends to be established later on. It should be noted that in bulk water the separation of the ions into stable hydrated configurations is complete after two to three water molecules have been interjected; that is, further separation does not change the

Table 1. Hydration Energies (in eV) of Water, Hydroxide, and Hydronium Ions in the Gas Phase and Adsorbed on OEG (Numbers in Brackets Are without BSSE Corrections)

$+(\text{H}_2\text{O})_n$	0	1	2	3
H ₂ O		0.206 (0.240)	0.696 (0.751)	1.290 (1.357)
OH [−] − H ₂ O	1.08 (1.16)	2.02 (2.17)	2.81 (3.02)	3.40 (3.66)
H ₃ O ⁺ − H ₂ O	1.57 (1.64)	2.59 (2.70)	3.41 (3.57)	4.00 (4.20)
CH ₃ (EG) ₃ OCH ₃		0.001	0.207	0.699
CH ₃ (EG) ₃ OCH ₃ − OH [−]	0.46 (0.48)	1.44 (1.52)	2.28 (2.43)	2.98 (3.18)
2CH ₃ (EG) ₃ OCH ₃ − OH [−]	0.79 (0.90)	1.6 (1.73)	2.45 (2.64)	2.98 (3.30)
3CH ₃ (EG) ₃ OCH ₃ − OH [−]				(3.33)

energetics anymore.²¹ That few water molecules are sufficient for the solvation of ions has been demonstrated in a recent compilation of cluster-ion solvation free energies.^{30,31}

2.2. Adsorption of Hydronium Ions on OEG. The extraction of metal ions by polyethers, including OEG from acidic media to an organic phase, is usually accompanied by the formation of stable complexes of the polyether with the hydrated proton.^{32,33} Frequently these complexes occur as cavities formed by the macromolecule surrounding the hydrated proton. In a recent paper,³⁴ such cavity complexes have been calculated within the Hartree–Fock approximation to extract bond lengths and also vibrational frequencies for comparison with infrared data in the gas phase. At the Hartree–Fock level, energies are not reliably estimated. In particular, it was shown that OEG 400 wraps around H₃O⁺ such that bonding with 8–10 oxygen atoms along the backbone of OEG takes place. These calculations were done at the Hartree–Fock level with a small basis set and with some constraints on the geometry to avoid dissociation of the water ion within the cavity.

Using the density functional theory, we have calculated the geometry and energetics of several conformers of (EG)₃ with a hydronium ion and with several additional water molecules. In analogy to the adsorption of neutral water on OEG, we find that the hydronium ion is most stably adsorbed on conformers of OEG with gauche defects which allow the formation of multiple strong hydrogen bonds. This is depicted in Figure 1. The binding energy is 3.57 eV. Most of this energy is needed to break the hydration shell of the hydronium ion in bulk water. Additional water molecules will stabilize the adsorption even further because they can cross-link over and under the plane depicted and also to the right of the molecule, enhancing the excess binding energy considerably, to the extent that it is larger than for the hydrated hydronium ion in bulk water. Noteworthy for our further deliberations is the size of this almost spherical cavity, about 8 Å in diameter.

The interaction of hydronium ions with a methyl endgroup (on either OEG or *n*-alkanes) is purely repulsive (apart from some weak attraction due to dispersion forces) due to the dominance of the interaction between the hydrogen atoms. On a terminal hydroxy group, the binding energy is about the same

(21) Geissler, P. L.; Dellago, C.; Chandler, D.; Hutter, J.; Parrinello, M. *Science* **2001**, *291*, 2121–2124.

(22) Khan, A. *Chem Phys. Lett.* **2000**, *319*, 440–450.

(23) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2001**, *105*, 11534–11540.

(24) Tunon, I.; Rinaldi, D.; Ruiz-Lopez, M. F.; Rivail, J. L. *J. Phys. Chem.* **1995**, *99*, 3798–3805.

(25) Xantheas, S. S. *J. Am. Chem. Soc.* **1995**, *117*, 10373–10380.

(26) del Valle, C. P.; Novoa, J. J. *Chem Phys. Lett.* **1997**, *269*, 401–407.

(27) Masamura, M. *J. Comput. Chem.* **2001**, *22*, 31–37.

(28) Trout, B. L.; Parinello, M. *Chem. Phys. Lett.* **1998**, *288*, 343.

(29) Trout, B. L.; Parinello, M. *J. Phys. Chem. B* **1999**, *103*, 7340–7345.

(30) Sprick, M. *Chem. Phys.* **2000**, *258*, 139–150.

(31) Tissandier, M. D.; Cowan, K. A.; Feng, W. Y.; Gundlach, H.; Cohen, M. H.; Earhart, A. D.; Coe, J. V. *J. Phys. Chem. A* **1998**, *102*, 7787–7794.

(32) Sharma, R. B.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 3913–3916.

(33) Junk, P. C. *Rev. Inorg. Chem.* **2001**, *21*, 93.

(34) Varnek, A.; Wipff, G.; Famulari, A.; Raimondi, M.; Vorob'eva, T.; Stoyanov, E. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 887–893.

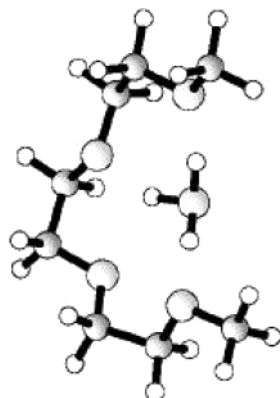


Figure 1. Encapsulation of H_3O^+ by methoxy-terminated (EG)₃.

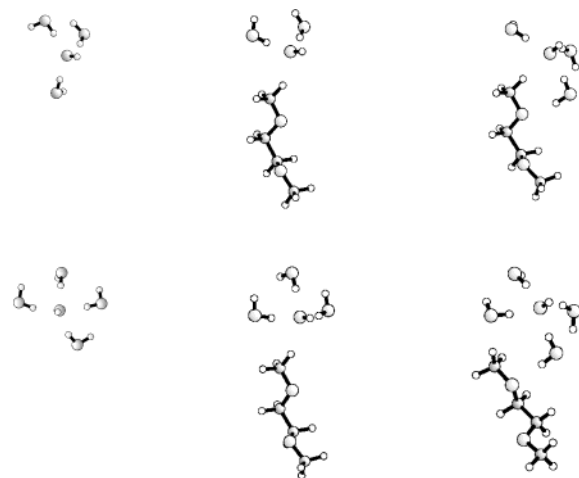


Figure 2. Optimal geometries of OH^- surrounded by water and on OEG for increasing numbers of water molecular (top to bottom). Left column: filling of the hydration shell for an isolated hydroxide ion. Center column: ion adsorbed on the methyl group. Right column: with water allowed to form cross-links to the oxygen of the methoxy group.

as with an isolated water molecule (in both situations, the binding is to the oxygen atom) but less than the interaction between the hydroxy group and a hydroxide ion.

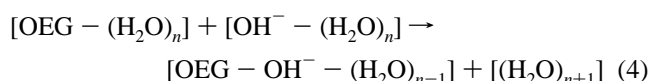
2.3. Adsorption of Hydroxide Ions on OEG. The negative charge of the hydroxide ion prevents it from adsorbing on the side of a OEG molecule due to the repulsion of the oxygen atoms along the backbone of the latter. Thus, adsorption can only take place at the headgroup. We begin with adsorption on the methyl (methoxy) group. In this case, the adsorption energy of OH^- on $(\text{EG})_3\text{-CH}_3$ is only 0.48 eV, that is, less than one-half of the binding energy of a water molecule on OH^- , see Table 1. The reason is that the charge on the hydrogen atoms of the methyl group is weaker than that on the hydrogen atoms of water. What is interesting is that the difference between the binding energy of the hydroxide ion OH^- on the methyl group or with H_2O decreases with an increasing number of water molecules surrounding it, that is, changing from 0.60 eV with no water molecule nearby to 0.42 eV with three water molecules forming part of the first hydration shell. In summary, adding additional water molecules to hydrate OH^- keeps the imbalance of about 0.4 eV against adsorption on the methyl group, see Table 1. The optimal adsorption geometries on OEG are depicted in Figure 2 for increasing numbers of water molecules. In the left column, we show the filling of the hydration shell for an isolated hydroxide ion, in the center column for this ion

Table 2. Excess Reaction Energy for the Transfer of a Hydroxide Ion from “Bulk” Water to OEG for Ontop Adsorption on One EG, Bridge Adsorption between Two EGs, and Hollow Site Adsorption between Three EG Strands, up to the First Hydration Shell

n	1	2	3
$\Delta E_{\text{B}}(\text{one EG})$ [eV]	−0.43	−0.11	0.04
$\Delta E_{\text{B}}(\text{two EG})$ [eV]	−0.04	0.09	0.25
$\Delta E_{\text{B}}(\text{three EG})$ [eV]	0.1	0.11	0.28

adsorbed on the methyl group, and in the right column with water allowed to form cross-links to the oxygen of the methoxy group.

The simplistic argument just presented is misleading. What we must consider is a Born–Haber cycle in which we start initially from two clusters, OEG in contact with some water molecules (mimicking bulk water) and OH^- in contact with some water molecules (again mimicking bulk water). The “reaction” entails the transfer of OH^- from the bulk water phase to OEG accompanied by a transfer of one water molecule from OEG into the bulk or, reformulated for clusters,



To favor the adsorption of OH^- on OEG, the excess reaction energy

$$\Delta E_{\text{B}} = E_{\text{B}}[(\text{EG})_3\text{OCH}_3 - (\text{OH})^- - (\text{H}_2\text{O})_{n-1}] +$$

$$E_{\text{B}}[(\text{H}_2\text{O})_{n+1}] - E_{\text{B}}[(\text{EG})_3\text{OCH}_3 - (\text{H}_2\text{O})_n] - E_{\text{B}}[(\text{OH})^- - (\text{H}_2\text{O})_n] \quad (5)$$

to go from left to right must be positive. To evaluate these energies, we need the binding energies of water clusters. The values given in Table 1 are in good agreement with the literature.¹⁹ We have only considered clusters with up to four water molecules, the reason being that isolated water clusters have a coordination quite different from that of bulk water. Whereas in the latter the average number of neighbors is between three and four, the lowest energy state for isolated water clusters consists of ring structures, at least up to pentamers, with only two bonds per molecule.

We have listed the excess reaction energies, calculated from eq 5, in Table 2.

It is striking that with more than two water molecules hydrating the OH^- attached to OEG, the reaction is favored, albeit by a small excess energy.

Before we proceed with further calculations, we must justify our exclusive use of binding energies as a criterion for reaction equilibria. It is known from previous work on the hydration of isolated hydroxide and hydronium ions that entropic corrections due to vibrational and rotational excitations in the cluster are small, leading to reaction free energies and enthalpies that are more or less uniformly shifted from the binding energies by about 0.02–0.04 eV. This shift is even smaller for the adsorption of ions on OEG because the reactants already contain clusters (and not individual molecules) so that the excitation spectra for the clusters of reactants and products are almost the same with changes on the individual clusters compensating each other. We have checked this by calculating the corrections in the free

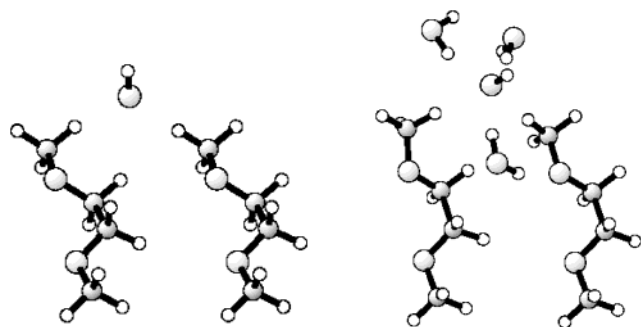


Figure 3. Adsorption and hydration of OH^- on two strands of methoxy-terminated OEG.

energies for the case with $n = 1$ in eq 5 and found that they amount to less than 0.02 eV at room temperature.

So far, we have looked at the adsorption of OH^- on the methyl group of a single $(\text{EG})_3$. Our ultimate aim is to understand the adsorption of water ions on an OEG SAM. In our next set of calculations, we looked at a cluster of three and four $(\text{EG})_3$ molecules with OH^- adsorbing on bridge and hollow sites, respectively. We have assumed that the molecules are spaced 5 Å apart as they would be on a gold substrate so that they can be in a helical conformation. Without any water present, we find that the binding energy roughly doubles to 0.89 and 0.94 eV, respectively, making the two sides of the reaction about equal in energy. Not much changes when we narrow the spacing and force the conformers to be all-trans; that is, the OH^- is pushed upward by about 0.2 Å and is bound less by about 0.1 eV.

Adding water to the system definitely pushes the reaction equilibrium to the right, but there is now a qualitative difference on whether the OEG is at different spacings. On the densely packed all-trans conformation, water can only adsorb on the outside of the OH^- , very much akin to what happened in the ontop position. On the other hand, we know that on the helical (or amorphous) conformer, water can adsorb on the side of $(\text{EG})_3$, building hydrogen bridges to the first two or three oxygens (from the top) of the OEG. This not only bridges two neighboring strands but also adds to the hydration of the ion. This situation is depicted in Figure 3. The corresponding excess energy is 0.25 and 0.28 eV for bridge and hollow sites, respectively.

To check how much the adsorption of OH^- on the terminal methyl group is influenced by the composition of the molecular chain (ethylene glycol versus n -alkane), we have done a calculation for its adsorption on methyl-terminated n -alkane. We find that the binding energy is 0.4 eV, down from 0.48 eV on methoxy-terminated OEG. This small change will not effect any of the statements about the importance of the hydration in the stabilization of the whole adsorption process, as quantified in the Born–Haber cycle. Thus, we conclude that there will also be a transfer of OH^- from bulk water to the methyl groups of SAMs made up of n -alkanes.

Our last set of calculations concerns the adsorption of hydronium and hydroxide ions on hydroxide-terminated OEG or n -alkane. We begin with a single OH^- ion (in the absence of water) approaching the hydroxide group. Because its negative charge is considerably larger than the partial charge of the hydroxide group, estimated at -0.2 by a Mulliken analysis, there will be a partial transfer of the hydroxide proton to the hydroxyl

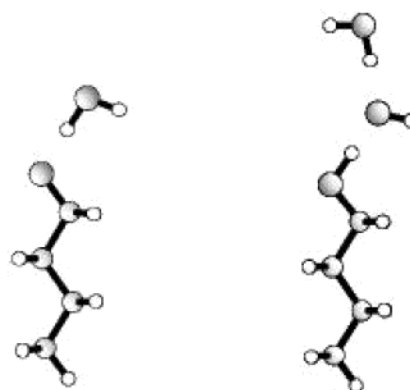


Figure 4. Adsorption and hydration of OH^- on hydroxide-terminated n -alkane.

ion, with a concurrent charge transfer from the hydroxyl ion to the OEG molecule, until the proton is halfway between the two oxygens, see Figure 4. This results in binding energies of 1.71 and 1.62 eV on the hydroxide-terminated $(\text{EG})_3\text{-OH}$ and n -alkanes, respectively. The presence of additional water breaks this symmetry in favor of stabilizing the hydroxide ion again, thus reducing the binding by at least 0.2 eV. This is not too surprising if we recall that a neutral water molecule adsorbs on the hydroxide group with a binding energy of 0.25 eV. The overall conclusion here is that OH^- will adsorb on hydroxide-terminated SAMs as well.

3. Discussion and Conclusions

We list our results from the ab initio calculations:

(1) Hydronium ions are encapsulated by isolated OEG molecules in water along the stretch of the molecule with a gauche defect.

(2) Hydroxide ions are adsorbed with most of their hydration shell intact on the methyl endgroup of isolated OEG. Indeed, energetically and geometrically very similar adsorption occurs when the methyl group terminates an alkane chain.

(3) The concurrent adsorption of both types of ions on the same OEG molecule is unstable because the two ions see each other with at most one water molecule in between. It is then energetically extremely favorable for the two ions to recombine into two neutral water molecules which themselves are bound at the gauche defect.

(4) On a cluster of narrowly spaced OEG or alkane molecules in their all-trans configuration, hydroxide ions adsorb preferentially above the bridge and hollow positions with more or less the same energetics and activation barriers of the order of $k_B T$ between them. Generalizing this result to a SAM (with predominantly these conformers, as is the case on a silver substrate), we recall their surfaces are hydrophobic. As a consequence, the adsorbed hydroxide ions are very mobile and can easily be moved around, for example, by an approaching negatively charged AFM tip or protein.

(5) On a cluster of OEG molecules, spaced so that their predominant conformers are helical or amorphous, the adsorption of hydroxide ions is stabilized by water that has penetrated into the SAM.

(6) An estimate of the surface density of hydroxide ions can be obtained from considering the lateral interaction between them. They repel each other by a Coulomb force modified by

the fact that they sit at the interface between two dielectrics with high (water) and low (SAM) dielectric constants. Also, screening by the hydronium counterions in water must be accounted for, as well as long-range charge-dipole interactions between the ion and the water molecules. Within an order of magnitude, we find a charge density of $1 \mu\text{C}/\text{cm}^2$.

(7) For a SAM on a metal, the adsorption of hydroxide ions is favored even more by the Coulomb attraction to the image charges in the metal

$$V_{\text{image}}(z) = -\frac{e^2}{4\pi\epsilon\epsilon_0 z} \quad (6)$$

where z is the distance from the ion to the metal surface, and ϵ is the dielectric constant of the SAM. For an n -alkane SAM, $z = n \times 1.3 \text{ \AA}$ and $\epsilon = 2.3$ so that for $n = 11$ the adsorption energy is lowered by about 0.15 eV, and less so for thicker SAMs. The resulting compressional force on the SAM is about 10 pN per ion. This is at the low end of the forces required to change the conformations of a macromolecule^{35,36} and results in a shortening of the length of an isolated chain by about 5% as long as the confinement due to the neighbors in the SAM allows such a contraction. Accounting for all accumulated OH^- charges of density σ , we find that the force on the SAM is $e\sigma/\epsilon = 80 \text{ pN}$ for $n = 11$. For an isolated alkane chain, this would lead to a shortening by 80%. This is obviously not possible in a dense SAM; nevertheless, some compression must occur. Its calculation would require detailed knowledge of lateral chain-chain interactions and of the packing constraints. We hope to return to this problem soon.

(8) The adsorption of hydronium ions can only proceed by penetration into the SAM. The resulting encapsulation by a single OEG strand requires so much lateral space that it can occur, at best, at defect sites in the SAM or in a less densely packed polymer brush. A further scenario is discussed below.

Our results can explain the electrokinetic measurements by Werner et al.^{12–14} which show an accumulation of negative charge on nonionic hydrophobic surfaces (fluoropolymers and alkanethiolate SAMs) and on hydroxide-terminated alkanethiolate SAMs. The negative charge originating from preferential hydroxide adsorption can also explain the reported long-range electrostatic forces measured between two $(\text{EG})_3\text{-OME}$ or an $(\text{EG})_3\text{-OME}$ and an alkanethiolate surface.^{2,4–6} According to our results, penetration of water into the SAM stabilizes the adsorbed hydroxide ion. That water penetration into the SAM seems to be a necessary requisite for resistance of the $(\text{EG})_3\text{-OME}$ monolayers to some proteins has been claimed (and supported by experiments) by Herrwerth et al.³⁸ However, protein resistance is too complex a phenomenon for a single process (water penetration) to explain it all.³⁹ Further, water

inside the SAM stabilizes the negative ion against lateral displacement. This can explain the experimental difference in long-range repulsion and attractive interaction between the OEG-terminated SAMs and the alkanethiolate monolayers, respectively. In the former case, the charges cannot be displaced by repulsive interactions due to the approach of the negatively charged tip, and so a net repulsion is measured, whereas mobile charges are displaced and the two surfaces attract due to hydrophobic forces.

The electrostatic repulsion between two $(\text{EG})_3\text{-OME}$ surfaces or an $(\text{EG})_3\text{-OME}$ surface and a hydrophobic tip can be screened out by a strong ionic solution, or can be neutralized by lowering the pH of the solution to values below pH 4. As will be shown in a separate publication, the pH dependence of the repulsive interaction between the $(\text{EG})_3\text{-OME}$ surfaces parallels the charge accumulation measured in electrokinetic measurements.¹⁰ Once the electrostatic repulsion is neutralized by ionic strength or pH, the interaction between these surfaces becomes attractive at a separation of approximately 10 nm, possibly due to solvation forces.^{9,37}

In conclusion, we would like to advance an idea on how the charging of a SAM might occur in situ when exposed to the aqueous solution. We consider a local configuration in the SAM consisting of a triangle of three OEG strands with a column of water molecules penetrating in the center. By a charge fluctuation, a proton is transferred from the topmost water molecule to the next one down. As in bulk water, the return process will be extremely likely, but there is a nonvanishing probability that the proton jumps further down the column and away from the hydroxide ion left on top. Indeed, for a SAM adsorbed on a metal, this process is aided significantly by the attraction of the proton to its image charge. This field-assisted proton-transfer reaction becomes more and more efficient as the proton cascades down toward the metal. The cascade eventually stops at the last oxygen plane of the three OEG strands. At this stage, the proton might end up as a hydronium ion which binds to the three nearest oxygens with an energy of about 4 eV (estimated from a Born–Haber cycle) plus the image interaction energy. Alternatively, the proton might attach itself to a (partially charged) oxygen atom on one OEG strand with about the same energy. All of the energetic estimates make field-assisted proton transfer plausible, although they cannot give us any information about reaction barriers in the kinetics. To get the latter, one would have to do a Carr–Parinello type calculation similar to the one recently reported for the autoionization of water.²¹

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(37) Hayashi, T.; Pertsin, A. J.; Grunze, M. *J. Chem. Phys.* **2002**, *117*, 6271–6280.

(38) Herrwerth, S.; Eck, W.; Reinhardt, S.; Grunze, M. *J. Am. Chem. Soc.*, in press.

(39) Kane, R. S.; Deschatelets, P.; Whitesides, G. M. *Langmuir* **2003**, *19*, 2388–2391.

(35) Oesterhelt, F.; Rief, M.; Gaub, H. E. *New J. Phys.* **1999**, *1*, 6.1–6.11.

(36) Kreuzer, H. J.; Grunze, M. *Europhys. Lett.* **2001**, *55*, 640–646.