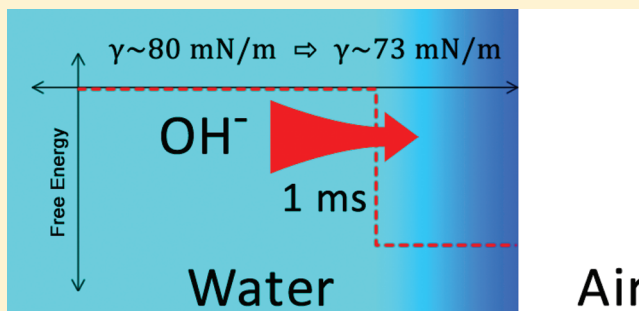


The Surface Relaxation of Water

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ABSTRACT: We examine three possible explanations for the millisecond relaxation time of the dynamic surface tension of water: the diffusion of surfactant contaminants from the aqueous phase to the surface, the reorientation of surface water molecules' dipole moments, and the buildup of a charged surface layer of hydroxide ions. The relaxation time expected for hydroxide is by far the closest to the measured time. Our model for the surface layer agrees with static equilibrium experiments and, as we show here, predicts the relaxation time. The results strongly imply that the equilibrium surface of water is highly charged by a flow of hydroxide to the surface. The model predicts that neither diffusion nor autolysis dominates and shows that both processes are needed to describe the relaxation of the surface tension. We find a salt and pH dependence of the relaxation time and propose further experiments.



INTRODUCTION

Rayleigh and subsequently Bohr developed the oscillating jet method for measuring surface tension.^{1,2} Schmidt et al. used this method and found that the surface tension of a freshly formed, pristine water/air interface is 80–100 mN/m, depending on the temperature, and that it relaxes to its equilibrium value in about 1 ms.³ We evaluate here explanations for this phenomenon. Surface tension relaxation has also been recently observed, again with the oscillating jet method.^{4–7} In one of these works, Kochurova and Rusanov found the surface tension relaxation time of water is about 0.6 ms.⁷ They also measured the surface potential of water using a smooth jet and found a similar relaxation time of 0.5 ms. Lyklema⁸ reprinted a figure from a different paper by Kochurova et al.,⁹ which shows that measurements using the oscillating jet method and the falling meniscus method agree. The agreement between independent methods shows that there is a restructuring process taking place in the first few milliseconds after creation of the surface.

The sign of the surface potential indicates that there is a buildup of negative charge at the surface of neutral water.¹⁰ We consider three possible explanations for this surface charge against the evidence from dynamic surface tension and potential measurements. The first explanation is that these charges come from surface adsorption of contaminant surfactants such as sulfonates and carboxylates dissolved in water and that the dynamic surface properties are caused by the diffusion of these surfactants to the fresh surface. The second explanation is that there is a preferred orientation of water dipoles at the interface,¹¹ perhaps slowed by some “icelike” structure as suggested by Kochurova and Rusanov.⁷ The third possible explanation is that hydroxide is attracted to the surface

and that the buildup of the layer via diffusion or autolysis takes about 1 ms.

Studies of Water's Surface Structure. We assess these three explanations because the composition of water near its surface, or near a hydrophobic interface, has been controversial. A variety of experiments point to adsorption of hydroxide as the source of this charge; others provide no evidence of hydroxide adsorption. We review here this work before analyzing the dynamic surface tension.

The experiments in favor of hydroxide adsorption include electrokinetic measurements of the ζ potentials of emulsions with no added surfactant,¹² of single oil drops, and of various gas bubbles.¹³ The pH dependence of the ζ potential is not itself in doubt; rather the origin of the charge it reveals has been debated.^{14–16} Zimmerman et al. reviewed the electrokinetic evidence and described the independence of hydroxide adsorption on the properties of a solid surface in contact with water.¹⁰ Djerdjev and Beattie showed that emulsification of hexadecane in water lowers the pH and that this lowering is consistent with one hydroxide ion per 3 nm² of hexadecane/water interface at about pH 9.¹² Any proposed surface charge mechanism must explain negative charge between the surface and the shear plane, about 2.5 nm deep, the lowering of pH on emulsification, and the pH dependence of the ζ potential. Our previous model for this phenomenon gives 20 $k_B T$ for the hydroxide's free energy of binding to a hydrophobe, and as discussed below, this energy has been confirmed spectroscopically.¹⁷

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Note that the evidence for hydroxide adsorption pertains to pH values between 2.5 and 9, with substantial surface charges above pH 5. As the ionic strength increases, image forces become rapidly more important,¹⁸ as do charge correlations.¹⁹ At concentrations above about 2 M, charge–charge correlations oscillate and the interface loses its double-layer structure.²⁰ It is unknown how these effects modify the layer at high ionic strength, though surface tension results indicate that image forces take over and produce a net repulsion of hydroxide before the pH reaches 12.²¹ We do not expect to see hydroxide adsorption at extreme concentrations.

On the other side of the argument, against hydroxide adsorption, most evidence is either spectroscopic or from molecular dynamics simulations. Spectroscopic methods have been used to identify various ions at surfaces,²² the main methods being sum-frequency spectroscopy (SFS),¹⁷ second harmonic generation (SHG),²³ and photoelectron spectroscopy (PS).²⁴ The strength of spectroscopic methods is that ions usually have distinctive spectroscopic signatures that when seen leave little doubt about their presence. Petersen and Saykally used SHG to study the surfaces of solutions of potassium and sodium hydroxides between pH 9 and pH 15.²⁵ The depth to which a spectroscopic method probes is not always clear, as noted by Petersen and Saykally. They saw no change in the SHG response between pH 9 and pH 14, which may be consistent with the saturated hydroxide surface layer predicted from electrokinetic measurements.¹² Of the spectroscopic studies that do not see adsorbed hydroxide, this study reaches the lowest pH in alkaline solution and so is the most telling.²⁵ Petersen and Saykally also fitted a Langmuir isotherm to their SHG results, neglecting electrostatics and all species other than hydroxide, at very high concentrations, and found the hydroxide repulsion from the interface that one would expect as image effects overwhelm the forces governing at low concentrations.^{14,21}

Winter et al. used photoelectron spectroscopy to study water and sodium hydroxide solutions at pH 13 and above.²⁴ They interpret their results as strong evidence against a surface enhancement of hydroxide. It is not clear if pure water was used in this study. A 0.05 M NaF solution was used as a reference to avoid charging effects. The concentration of hydroxide within ~1 nm of the interface is expected to be about 0.5 M near pH 9.^{12,14} The hydroxide solutions studied by Winter et al. have bulk concentrations similar to the expected surface hydroxide concentration, so one would not expect to see a significant surface enhancement. Rather, the ionic strength is so high throughout the bulk that correlation and image effects must overwhelm other forces. The Debye length at the lowest hydroxide concentration studied by Winter et al. is about 1 nm: clearly the layer structure cannot at all resemble that at pH 9 and below. Winter et al. also suggest that the surface charge reported by Djerdjev and Beattie¹² is implausible because it would require “an unrealistically thick layer of several millimetres completely devoid of OH[−]_(aq)”. Hydroxide is formed by the autolysis of water, so this criticism is flawed. A fuller criticism of the work of Winter et al. has been published,^{26,27} as have their responses.²⁸ The debate continued in later work.^{15,16} Tian and Shen used phase-sensitive sum-frequency spectroscopy to study the interfaces between electrolyte solutions and a hydrophobe, octadecyltrichlorosilane. They confirmed the binding free energy of hydroxide to the hydrophobe, 20 $k_B T$, obtained by fitting to ζ potentials.¹⁴

Molecular dynamics simulations appear compelling, but are only practical at unrealistically high ionic strength and are limited by the accuracy of their force field. We are aware of no classical molecular dynamics simulation of hydroxide's interaction with a surface or hydrophobic interface that uses a model known to describe correctly the interaction of a hydroxide with its solvation shell, in particular its coordination number.^{26,29} One study using density-functional theory of 215 water molecules reported a weak hydroxide adsorption, with a binding free energy of about $k_B T$, raising the possibility that the size of the simulation cell is an important factor.³⁰ Measurements of the surface tension as a function of pH would seem the most direct method of resolving the controversy, but these are only available at high concentrations of hydroxide, where repulsion of the hydroxide from the interface is expected.²¹ Note that on the acid side of pH 7 the surface tension is predicted to be independent of pH²⁶ and on the basic side the surface tension grows in proportion to the hydroxide coverage,²⁸ but the magnitude of the effect is small. We are aware of no static surface tension measurements that reveal the surface composition near pH 7.

■ DIFFUSION OF SURFACE-ACTIVE MOLECULES

Dynamic surface tensions of various surfactant solutions have been measured. The rate of their buildup at the surface frequently depends on diffusion from the bulk.^{4,31–34} Previous work has found there is a simple relaxation time estimate for this buildup:^{35–37}

$$\tau_D = \frac{(\Gamma/c)^2}{D} \quad (1)$$

where Γ is the equilibrium surface coverage of the surfactant, c is the bulk concentration of the surfactant, and D is the diffusion coefficient. This is the time taken by a surfactant molecule to diffuse a distance of Γ/c , which is the width of the smallest bulk region capable of supplying enough surfactant to fill the layer to equilibrium. By treating the surface as a Langmuir monolayer, the ratio Γ/c can be expressed in terms of the adsorption equilibrium constant, the maximum surface coverage, and the bulk concentration. Decreasing the concentration of surfactant always increases the diffusion time given by eq 1, because it takes longer for enough surfactant to reach the surface. Experiments show this qualitative behavior, and eq 1 is in good agreement with experimental relaxation times.^{4,31–34} For example, when applied to 0.9 mM Triton X-100 solution, the experimental and calculated relaxation times are both about 14 ms; when this concentration is decreased to 0.3 mM, the experimental and calculated relaxation times are both about 40 ms.⁴

We now consider the adsorption from water solution of contaminant surfactants, such as carboxylic acids and sulfonates, as a possible cause for the dynamic surface tension of pure water. The possibility of surfactants already present at some surfaces is discussed below. The dynamic surface tensions of these surfactants have been measured at concentrations between 0.1 and 10 mM, and the diffusion times are found to be between 10⁴ and 1 s.^{35,38,39} For contamination in water, the concentration is expected to be lower than these experimental concentrations; thus, the diffusion times are expected to be even longer. The measured relaxation time of pure water is about 1 ms. It is not plausible that enough contaminant surfactant could be present to account for the

short observed relaxation time. Furthermore, it would have a significant and measurable effect on the equilibrium surface tension, and it is even more unlikely that every measurement of surface tension could have been affected by the same contaminant in the same amount. Therefore, we dismiss the buildup of surfactant impurities as a possible cause of the dynamic surface properties of water.

RELAXATION OF DIPOLES AT THE SURFACE

It has been proposed that the negative surface charge is due to a preferred orientation of water at the surface.¹¹ The reorientation time of dipoles at a fresh interface would thus give rise to the surface relaxation of water. Such a process would have a time scale similar to the bulk dielectric relaxation time scale, which is about 8 ps.⁴⁰ Kochurova and Rusanov speculated that evaporative cooling might lead to an icelike surface layer with a slower dipole reorientation time, but this is an ad hoc explanation.⁷ We are aware of no experiment or simulation that directly supports the presence of an icelike layer or other constrained structure, and recent spectroscopic and theoretical work provides strong evidence against it.⁴¹ Lyklema “refrained” from suggesting an explanation, noting that the observed millisecond relaxation time is well established.⁸

Some structure less ordered than the icelike structure is likely to be present, for example, free O–H bonds pointing away from the bulk. It is difficult to estimate without a clear relaxation mechanism, but a slowing of the dielectric relaxation time near the interface by 8 orders of magnitude seems unlikely. A recent review describes a slowing of water’s orientational relaxation time from 2.6 to 15 or 20 ps,⁴² a factor of 8, not the $\sim 10^8$ needed to explain the relaxation of surface tension.

HYDROXIDE ADSORPTION

The third explanation considers the buildup of hydroxide in a layer at the surface. The ζ potential of air bubbles in water has a strong pH dependence,^{43,13} and experiments point to hydroxide’s attraction to the oil/water interface^{12,14} (see the discussion above). The hydroxide diffuses more quickly than other species except the proton and can be created via autolysis near the interface, so it is more likely to give millisecond relaxation than are impurity surfactants. The isoelectric point of the air/water interface is found to be between pH 2.5 and pH 4.^{12,44} The ζ potentials of other hydrophobes such as oil drops, or polystyrene surfaces, are very similar.^{10,12,44}

We have proposed an explanation for this attraction of hydroxide to the surface.¹⁴ We argued that the hydroxide ion suppresses correlation between fluctuating water dipoles near the ion and is thus repelled from the bulk by a dispersion force that arises from correlations between the fluctuating conformations of permanent dipoles. By fitting a model for this effect to air/water interface data, we found a surface-binding free energy, ω , of $16 k_B T$; and by fitting to data on oil/water interfaces, we found $20 k_B T$. The value of $\omega = 20 k_B T$ was later confirmed by phase-sensitive sum-frequency vibrational spectroscopy.¹⁷ These two energies give isoelectric points at pH 4 and 3, respectively, corresponding to the range in the experimental data discussed above. Recent work by Tabor et al. shows that this variation in isoelectric point is due to dissolved carbon dioxide.⁴⁴ The dynamic surface tension measurements discussed here were done in air, so we expect a binding energy of $16 k_B T$ to give a better model. Apart from

the estimate of this binding free energy, we do not make use of the earlier model.

RATES OF DIFFUSION AND AUTOLYSIS

Before making an estimate of the relaxation time that includes the effects of both autolysis and diffusion, we estimate the relaxation times for these two processes separately. The diffusion coefficient of the hydroxide ion⁴⁵ is $5.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. If all the hydroxide on the surface diffuses from the bulk, then the depletion layer Γ/c would be as large as 5 mm for neutral water, which corresponds to a relaxation time of approximately $\tau_D \approx 5000 \text{ s}$ (see eq 1). Autolysis must play an important role in the observed millisecond relaxation.

We now estimate the relaxation time by assuming it is due to autolysis only and without using a Langmuir model for the surface layer. Below we give a more sophisticated and realistic theory that uses a Langmuir model to place an upper limit on the possible surface coverage by hydroxide. The bimolecular rate constant for the recombination of protons and hydroxide ions is $k_r = 1.35 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$.⁴⁵ The rate equation is

$$\frac{dc_-}{dt} = \frac{dc_+}{dt} = k_r K_w - k_r c_- c_+ \exp(-\omega/k_B T) \quad (2)$$

where c_- is the concentration of hydroxide, c_+ is the concentration of protons, $K_w = 10^{-14} \text{ M}^2$, k_B is the Boltzmann constant, and T is the absolute temperature. Solving eq 2, and assuming a sufficiently large ω , we obtain the autolysis-only relaxation time:

$$\tau_A = \frac{e^{\omega/k_B T}}{k_r \sqrt{\Delta c^2 + 4e^{\omega/k_B T} K_w}} \quad (3)$$

where $\Delta c = c_+ - c_-$ is the difference between proton and hydroxide concentrations in the surface layer. We have used $\omega = 16 k_B T$, the value obtained by fitting to surface tension measurements for the air/water interface (see the discussion above).¹⁴ We use conditions approximating those studied by Kochurova and Rusanov, pH 6.4 and $4 \times 10^{-5} \text{ M}$ monovalent salt. The measured surface coverage of hydroxide is about 0.33 nm^{-2} at about pH 9.¹² Assuming that this reflects the closest approach of hydroxide in the layer, we estimate the surface concentration difference to be $\Delta c = 0.32 \text{ M}$ and find the relaxation time τ_A is 0.3 ms. An alternative approach is to use the fits to experimental data described below to obtain Δc . That approach is not quite consistent, but does give relaxation times in the millisecond range, e.g., 5 ms for the parameters used in Figure 1. This estimate of 0.3 ms is closer by orders of magnitude to the experimental value of 0.6 ms than those obtained for alternative explanations for the dynamic surface tension. A better treatment, including the effects of diffusion into and out of the surface layer, follows.

EQUILIBRIUM STRUCTURE

Outside the surface layer we simplify our model by neglecting any force on the ions other than the electrostatic force. We call the region immediately outside the hydroxide layer the subsurface. In an earlier paper we used a more advanced treatment that included the dispersion and image forces on each ion.¹⁴ Our approach here is to fit our model for the surface structure to static equilibrium experiments and then to estimate the surface relaxation time without further fit.

Denoting ϕ as the electrostatic potential in the subsurface, we model the surface as an infinite plane so that $\phi(x)$ is only a function of the depth x . The electrostatic potential is $\phi_0 = \phi(0)$ at the surface layer. We use the Poisson–Boltzmann equation:

$$\frac{d^2\phi}{dx^2} = \frac{8\pi Q}{\epsilon}(\tilde{c}_+ + \tilde{n}_+)\sinh(\beta Q\phi) \quad (4)$$

where \tilde{c}_+ denotes the concentration of protons in the bulk, \tilde{n}_+ denotes the concentration of monovalent salt cations in the bulk, and the other quantities have already been defined. We use atomic units throughout unless otherwise indicated. This equation has a convenient analytic solution. We include the hydroxide-stabilizing energy ω in the surface layer (i.e., $-\omega$ is the binding free energy of a hydroxide in the surface layer), and we denote the thickness of the surface layer Δ . We neglect species other than protons and hydroxide in the surface layer for simplicity.¹⁴ We assume that the two ions in the surface layer obey Langmuir isotherms, and a third equation, derived from Gauss's law, connects the electrostatic potential ϕ to the surface concentration. Note that we use a Langmuir isotherm because it places an upper limit on the ion concentration near the interface, an essential feature of any double-layer model.

We do not think it likely that the layer of hydroxide is confined to a monolayer, and our earlier model made no special assumptions about the surface layer,¹⁴ but rather predicted the hydroxide concentration to be within about ~ 1 nm of the interface. The two approaches make very similar predictions of static structure. Experimental ζ potentials are the mean electrostatic potentials at the shear plane about 2.5 nm from the interface and show that the negative hydroxide charge is concentrated within this 2.5 nm of the interface. This negative charge is balanced by a diffuse layer of positive charge extending roughly the Debye length deeper than the shear plane. The model for the coverages may be summarized as

$$\bar{\Gamma}_+ = \frac{\tilde{c}_+ \Delta e^{-\beta\phi_0}}{1 + \nu \tilde{c}_- e^{\beta(\phi_0 + \omega)} + \nu \tilde{c}_+ e^{-\beta\phi_0}} \quad (5)$$

$$\bar{\Gamma}_- = \frac{\tilde{c}_- \Delta e^{\beta(\phi_0 + \omega)}}{1 + \nu \tilde{c}_- e^{\beta(\phi_0 + \omega)} + \nu \tilde{c}_+ e^{-\beta\phi_0}} \quad (6)$$

$$\left. \frac{d\phi}{dx} \right|_{x=0} = -\frac{4\pi Q}{\epsilon}(\bar{\Gamma}_+ - \bar{\Gamma}_-) \quad (7)$$

where “+” denotes quantities related to protons, “−” denotes quantities related to hydroxide, $\bar{\Gamma}_\pm$ are the equilibrium surface coverages, and \tilde{c} is a bulk concentration. The potential and its gradient at $x = 0$ are connected by the solution to eq 4 under the boundary condition that the potential vanish as x becomes large. Equations 5 and 6 can be likened to a two-species competitive Langmuir adsorption scheme,⁴⁶ where ω , Δ , and ν serve the same purpose as ordinary Langmuir isotherm parameters. ν^{-1} is the maximum volumetric density of ions in the surface layer. The relationship $\Gamma_{\max} = \Delta/\nu$ emerges by comparison with the ordinary Langmuir equation, where Γ_{\max} is the maximum possible surface coverage. Combining eqs 4–7, ϕ_0 can be calculated from the quantities \tilde{c}_+ and \tilde{n}_+ and parameters ω , ν , and Δ .

It is important to note that though the pH is uniform from the bulk to the interface, the concentrations of hydroxide and hydronium vary. The best definition of the pH is in terms of

activity, not concentration, and uniform activity for each species is a consequence of thermodynamic equilibrium.^{14,45}

This model differs from the one used by two of us in studying the affinity of hydroxide for interfaces between water and hydrophobes.¹⁴ We have checked that it performs just as well in describing the static structure of the interface. In fact, so close is the correspondence between the two models that the parameters from our previous paper may be used without further fit in the region of interest for pH < 7. For example, using the parameters obtained before for the oil/water interface in eqs 5–7 gives very similar ζ potentials. At higher pH this simple correspondence fails, and ζ potentials estimated this way tend to be too high, because the two models handle high potentials in different ways. The parameters used here are related to those used in our earlier work by the equations $\omega = \Omega k_B T$, $\nu = \rho_0 a^3$, and $\Delta = a$. The Langmuir model used here is preferable for this work because it both lends itself more easily to the calculation of relaxation times and also more closely resembles models used in the past to study dynamic surface tension.⁴⁷

Our earlier model for hydroxide adsorption used a modified Poisson–Boltzmann equation to describe the electrostatics and was fitted to experiment to find $\omega = 20 k_B T$ at the oil/water interface and $\omega = 16 k_B T$ at the air/water interface.¹⁴ Measured isoelectric points for the interfaces between water and hydrophobes range from about pH 2.5 to pH 4.^{12,13,44,48} Using eqs 5–7, this range of isoelectric points corresponds to a range of ω between ~ 20 and $\sim 16 k_B T$, respectively. A fit to the salt dependence of surface tensions gives $\omega = 16 k_B T$,¹⁴ and recent force measurements show no repulsion between air bubbles at pH 4.⁴⁹ Furthermore, the work of Tabor et al. indicates an isoelectric point for the air/water interface at pH 4 and suggests dissolved surface-active carbon dioxide as the explanation for the variation.⁴⁴ Taken together, these measurements of ζ potential, surface tension, and force support parameter values for the air/water interface of $\omega = 16 k_B T$; $\Delta = 13.6$ bohr, and $\nu = 2.5 \times 10^3$ bohr³. For completeness we fit the model for static structure to various experiments and consider a wide range of parameters (see Table 1).

■ DYNAMICS AT THE SURFACE

We first consider the relaxation times in the subsurface, the region just outside the surface layer. In this region we assume that the only force on ions is electrostatic. We use eq 3 with ω , the change in a hydroxide's free energy due to surface interaction, set to 0. The maximum value of τ_A is obtained from eq 3 when $\Delta c = 0$ and $\tau_A^{\max} \approx 0.07$ ms. As hydroxide becomes depleted from the subsurface, this relaxation time becomes faster. This shows autolysis in the subsurface occurs significantly faster than relaxation of the surface tension itself; that is, hydroxides are quickly reproduced in the subsurface. Under the conditions of interest to us, subsurface autolysis is much faster than the surface tension relaxation.

Buildup of an electrical double layer is required for charge neutrality of the interface overall. The Debye length of pure water, Λ_0 , is given by

$$\Lambda_0^{-2} = \frac{4\pi\beta}{\epsilon} 2\rho_0 Q^2 \quad (8)$$

where $\beta = 1/k_B T$, ϵ is the relative permittivity of water, $\rho_0 = K_w^{1/2}$ is the number density of hydroxide in pure water, and Q is the magnitude of the ion's charge; in this case it is the elementary charge. Λ_0 evaluates to approximately 1 μm , and the

time scale for this Debye-length diffusion is approximately 0.2 ms; thus, ions can quickly diffuse into the subsurface. This time becomes dramatically smaller as salt is added or the pH is altered. For Kochurova and Rusanov's water with 40 μM salt,⁷ the Debye-length diffusion time scale is about 0.5 μs . This process is also far faster than the surface tension relaxation under the conditions of interest to us.

From these estimates, we conclude that autolysis and diffusion in the subsurface have much faster time scales than the millisecond relaxation observed at the surface. We can thus safely neglect any dynamic properties of the subsurface and assume that the distributions of hydroxide and protons in the subsurface do not deviate significantly from the static equilibrium structure. We are seeking the last exponential relaxation to the equilibrium structure, so this approximation holds.

Four processes contribute to the changes in the concentrations of protons and hydroxide in the surface layer: creation within the layer, annihilation within the layer, diffusion into the layer, and diffusion out of the layer. The rate equations below are expressed as sums of these four terms in the above order. This model for dynamic surface tensions is widely used,³³ though we have generalized it to include autolysis. We assume the concentration of ions other than hydroxide and protons in the surface layer is negligible. We assume also that, to escape the layer, an ion must diffuse a distance Δ .

$$\frac{d\Gamma_+}{dt} = k_r K_w L^2 \Delta - \frac{k_r}{\Delta} \Gamma_+ \Gamma_- e^{-\beta\omega} + \frac{D_+}{\Delta} L e^{\beta Q \phi_0} \tilde{c}_+ - \frac{D_+}{\Delta^2} \Gamma_+ \quad (9)$$

$$\begin{aligned} \frac{d\Gamma_-}{dt} = & k_r K_w L^2 \Delta - \frac{k_r}{\Delta} \Gamma_+ \Gamma_- e^{-\beta\omega} \\ & + \frac{D_-}{\Delta} L e^{-\beta Q \phi_0} \tilde{c}_- - \frac{D_-}{\Delta^2} \Gamma_- \end{aligned} \quad (10)$$

Here $L = 1 - (\nu/\Delta)(\Gamma_+ + \Gamma_-)$ accounts for the reduction of the concentration of water molecules as the number of ions in the surface becomes large. It does not deviate very far from 1, but is included for consistency. Recall that we have assumed an ion must travel a distance Δ to escape, so the rate constant for this process is D_{\pm}/Δ . Since diffusion of hydroxide and protons takes place via the Grotthuss mechanism, the fraction of available sites for diffusion is equal to the fraction of water molecules available for ionization, L .

To extract the relaxation time scale for this dynamical system, we expand Γ_+ and Γ_- about equilibrium and examine the first-order perturbations. The problem has now been reduced to a two-dimensional, linear dynamical system and yields two exponentially decaying modes of solution, obtained as eigenmodes of the matrix of coefficients of the deviations from equilibrium. These are

$$\delta\Gamma_+ = \Gamma_+ - \bar{\Gamma}_+ = a\sqrt{1 - S^2} e^{-t/\tau_s} + bF e^{-t/\tau_F} \quad (11)$$

$$\delta\Gamma_- = \Gamma_- - \bar{\Gamma}_- = aS e^{-t/\tau_s} + b\sqrt{1 - F^2} e^{-t/\tau_F} \quad (12)$$

where $((1 - S^2)^{1/2}, S)$ and $(F, (1 - F^2)^{1/2})$ are eigenvectors of the modes normalized to a magnitude of 1 and a and b are amplitudes of the modes. These relaxation time scales τ_s and τ_F do not depend on the amplitude of the relaxation because these equations are linear in the deviation from equilibrium.

RESULTS AND DISCUSSION

Of the two decaying solutions in eq 10, the first has a relaxation time τ_s in the millisecond range, and the relative rate of proton buildup compared to hydroxide buildup is $(1 - S^2)^{1/2}/S \approx 10^{-5}$, reflecting the proportionality found in eqs 5 and 6. The second mode of solution F has a much faster relaxation time of $\tau_F \approx 10^{-10}$ s and is proton-dominated with $F/(1 - F^2)^{1/2} \approx 10^8$. As its relaxation time is much faster than the first mode, its effect on the dynamics at the millisecond scale is negligible. This then implies that the millisecond buildup of ions at the interface is almost entirely dominated by the first mode. We examine only the first mode in more detail. Experimental dynamic surface tension data fit well with a single exponentially relaxing mode.^{8,7}

Figure 1 shows the variation of the relaxation time we predict, τ_s , with pH and added monovalent salt concentration.

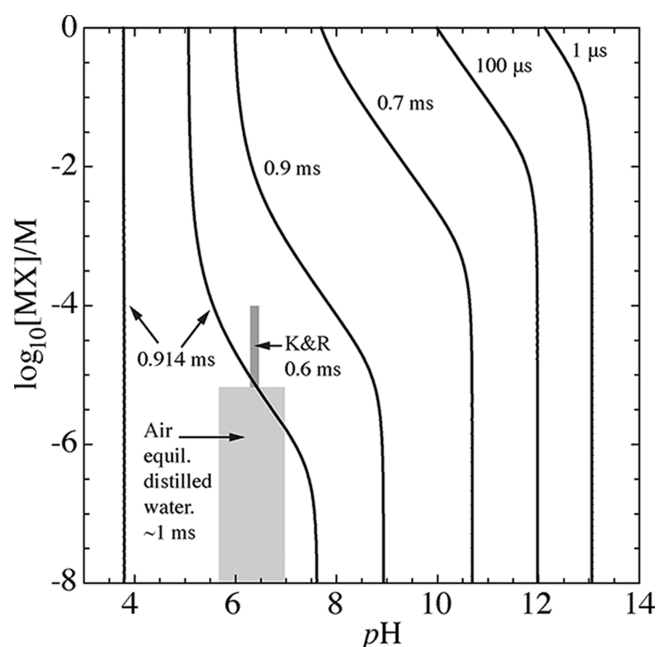


Figure 1. Contours of the predicted surface relaxation time, τ_s , for water at various pH values and added salt concentrations. The parameters chosen are $\omega = 16 k_B T$, $\Delta = 13.6$ bohr, and $\nu = 2.5 \times 10^3$ bohr³ (see the text). The darker shade indicates conditions reported by Kochurova and Rusanov, who found 0.6 ms.⁷ The ~ 1 ms relaxation time reported by other authors is not accompanied by conductivity and pH measurements,^{3–6} but is assumed to be a measurement for distilled water in air, illustrated with a paler shade.

The parameters used here are those obtained from fits to surface tensions of electrolyte solutions¹⁴ and supported by independent ζ potential^{44,48} and force⁴⁴ measurements, as described above: $\omega = 16 k_B T$, $\Delta = 13.6$ bohr, and $\nu = 2.5 \times 10^3$ bohr³. Experiments on the dynamic surface tension of water are typically performed using distilled water. Due to exposure to atmospheric CO₂, the pH of air-equilibrated water tends to be less than 7, and this water can contain as much as 40 μM ions as in Kochurova and Rusanov's water.⁷ This value is calculated from measured conductivities and assuming an averaged limiting molar conductivity.⁵⁰ According to the International Standard ISO2456, water used in the surface sciences should be doubly distilled to a conductivity less than 1 $\mu\text{S cm}^{-1}$, which is approximately 7 μM ions.⁵¹ Pashley et al. found that an ISO-compliant sample of water has a pH of 5.7 when equilibrated in

air.⁵² References to distilled water thus assume the typical conditions of pH 5.7 and $[MX] = 7 \times 10^{-6}$ M. In Figure 1 the region between pH 5.7 and pH 7 is shaded to indicate the likely effects of dissolved carbon dioxide.

The parameters may also be determined by fitting ϕ_0 calculated from eqs 5–7 to experimental ζ potentials of an interface varying with pH.^{10,12,44} Results of such fits are given in Table 1. We chose two approaches. First, we used the measured

Table 1. Predicted Surface Tension Relaxation Times^a

fit method	system	ref	$\omega/k_B T$	τ_s/ms
	air	14	16	0.91
1	N ₂	13	16	7.2
1	N ₂ or Ar	44	16	4.9
1	air	44	13	0.24
1	air	48	15	1.9
2	N ₂	13	18	3.0
2	N ₂ or Ar	44	17	2.0
2	air	44	14	0.10
2	air	48	16	0.77

^aPredicted surface tension relaxation times and the parameters obtained from earlier work (top row) and from the two fit methods described in the text. As expected, the relaxation times are closer to the experimental value of ~ 1 ms for fits to data on the air/water interface. We note that all the estimates given in this table are closer to experimental values than estimates based on competing explanations.

surface coverage¹² of 0.33 nm^{-2} to estimate $\Delta = 56.7$ bohr and allowed ω to vary. Second, we fixed $\Delta = 13.6$ bohr, obtained as described above, and allowed ω to vary. Results for these methods, numbered 1 and 2, respectively, are given in Table 1. The fitted curves are shown in Figure 2. All fits are obtained using the nonlinear least-squares fit as implemented in Mathematica version 8.0. The largest standard error for any $\omega/k_B T$ result reported in Table 1 was 0.7. We fit to a variety of data from the literature on air/water interfaces and on interfaces between water and gases not containing carbon dioxide. In all cases, we concentrated on data for pH < 7. Data for ζ potentials at pH > 7 are widely scattered, and errors, where available,⁴⁴ are so large that these data have little effect. The value of ϕ_0 depends only weakly on Δ and ν around pH 6, which is the region of interest for the dynamic surface tension measurements discussed here.

Table 1 also gives estimates of the surface relaxation times using eqs 9 and 10 and the various fits to ζ potentials shown in Figure 2. All estimates based on the buildup of hydroxide at the surface are much closer to the experimental values of 0.6–1 ms than any estimates based on competing explanations. In particular, under the conditions studied by Kochurova and Rusanov, who found 0.6 ms, we find 0.9 ms.

The salt concentration affects the Debye length and the electrostatic potential in the layer, so the relaxation time changes as the salt concentration is altered. The contributions to τ_s of the terms in eqs 9 and 10 show that diffusion makes a much more important contribution to the buildup of hydroxide than autolysis. This is expected as autolysis is a relatively slow process, and as the surface becomes increasingly charged, production of ions within the surface layer will become increasingly difficult. A likely mechanism is that hydroxide–proton pairs are created via autolysis in the subsurface and hydroxide then diffuses into the surface. Once hydroxide adsorbs onto the surface layer, the stabilization energy $\exp(\omega/$

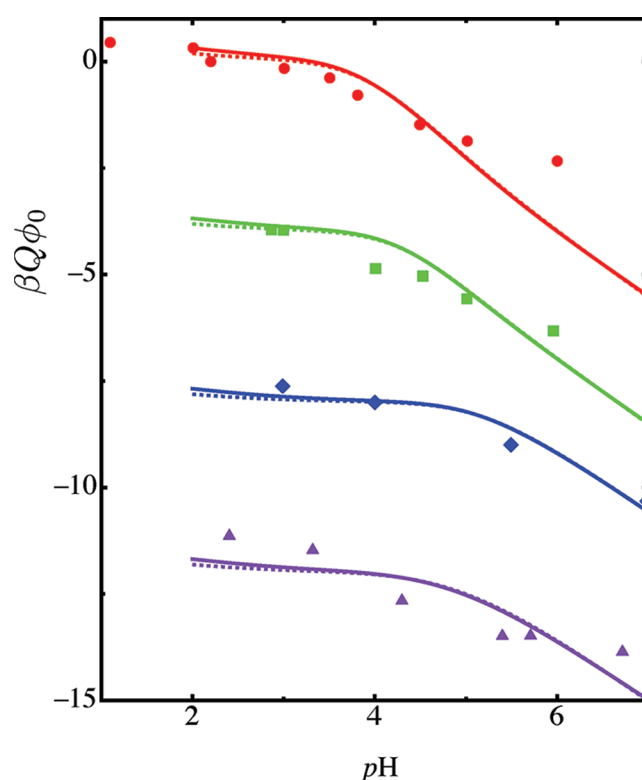


Figure 2. All fits reported in Table 1. The results of method 1 are the solid lines; the results of method 2 are the dotted lines. The different fits are shifted vertically by multiples of 4 for clarity. The gases used in the experiments, and sources for the data, for each set of points are as follows: circles, N_{2(g)}, from ref 13; squares, Ar_(g) and N_{2(g)} data combined, from ref 44; tilted squares, air, from ref 44; triangles, air, from ref 48.

$k_B T$) traps them inside the layer, and thus, there is a buildup. Protons on the other hand are not trapped within the layer, and thus, the concentration of protons remains within an order of magnitude of the bulk concentration.

Roger and Cabane found that fatty acid impurities in hexadecane can adsorb and then react with hydroxide.⁵³ For the air/water interface, we have shown here that diffusion of surfactant impurities from the bulk aqueous solution to the interface is too slow to account for the observed millisecond relaxation. We do not rule out surfactant impurities already present at the interface, as for the emulsions reported by Roger and Cabane. The model presented here assumes hydroxide binding to the surface, but makes no assumption about its mechanism.

CONCLUSION

Of the three possible explanations for the surface potential and dynamic surface tension of water that we have considered, the flow of hydroxide to the surface agrees best with the experimental value of ~ 1 ms by a considerable margin. Even at concentrations as high as 10 mM, typical surfactant impurities flowing to the surface from the bulk water would give a surface tension relaxation time of about 1 s, larger than the experimental value by about 10^3 . The orientational relaxation time for the dipole moments of water molecules at the surface is closer to 10 ps, and the presence of icelike structures at the surface of water is not supported by other experiments or simulations; rather recent experimental and

theoretical work failed to detect such a structure.⁴¹ It is difficult to see how surface dipoles could relax 10^8 times more slowly than those in the bulk to give the experimental relaxation time. Interfacial orientational relaxation times have been observed to slow by a factor of 8.⁴² The buildup of hydroxide has a predicted relaxation time of about 1 ms, close to the measured value.

Our result is robust in that it does not arise from a single model and that the hydroxide relaxation time remains closest by far to the experimental value whether we take parameters from our previous work or from fits to a variety of experimental data. Even at first glance, hydroxide is the species most likely to produce millisecond relaxation, as it diffuses quickly in water and can be created near the interface via autolysis. We have taken models of hydroxide adsorption that fit experiments on static equilibrium surface structure, and from these we estimate the slowest relaxation time in the buildup of the hydroxide layer without any further fit. We note also that the argument in this paper depends on measurements that point to hydroxide adsorption, but not on any assumptions about the force behind this adsorption. We find a simple estimate based on the kinetics of autolysis with stabilized hydroxide, eq 2, gives good agreement with experiment. A more sophisticated model, well supported by other authors' work on many surfactants, and generalized by us,³³ also gives estimates close to ~ 1 ms. The significance of our results is that, for any choice of model for the surface that fits with an experiment, the predicted relaxation time is far closer to the experimental value than for competing explanations. We think the best model is the one taken from fits to surface tension data¹⁴ and supported by ζ potential and force measurements. This model of static surface tension gives a relaxation time of 0.9 ms.

Some have argued that hydroxide is not the cause of the surface charge. Vácha et al. presented experimental evidence that the surface charge does not have a pH dependence at pH > 7.¹¹ This is consistent with our model for the interface. It can be shown that, by substituting any reasonable parameters into eq 6, the surface concentration of hydroxide saturates at high pH and the pH dependence of this surface charge is only significant near the isoelectric point. The adsorption of hydroxide is supported by measurements of ζ potentials,¹³ by the lowering of the pH on emulsification,¹² by phase-sensitive sum-frequency vibrational spectroscopy,¹⁷ and, as shown here, by the measured dynamic surface tension. Other explanations for the surface relaxation have estimated time scales that are several orders of magnitude away. Our calculations predict that the relaxation time should fall significantly with increasing ionic strength. We suggest experiments at high pH or ionic strength as a further test.

Our results clearly imply that the equilibrium surface tension of water, 72 mN/m at 298 K, is that of an interface charged by the flow of hydroxide and not that of the pristine air/water surface as has sometimes been assumed.

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Notes

The authors declare no competing financial interest.

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