



## Organic ions at the air/water interface

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### ABSTRACT

Direct spectroscopic evidence of the presence of organic phenolate ions at the air/aqueous interface has been established using the nonlinear spectroscopic technique of vibrational sum frequency generation (SFG). By probing the phenol C–OH and the phenolate C–O<sup>−</sup> vibrational stretches, which occur in the range of 1200–1300 cm<sup>−1</sup> and are distinguishable, we have succeeded in determining the identities of the chemical species present at the air/aqueous interface of phenol–phenolate solutions at bulk pH values ranging from 3.2 to 13.2. We have found that in addition to phenolate ions that phenol is present at the interface at high bulk pH values.

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### 1. Introduction

Understanding the propensity of ions for the air/water interface is of fundamental and practical importance. This is illustrated by the facts that about two-thirds of the earth's surface is the ion rich air/water interface and that many reactions in nature involve charged species and occur most readily at the interface – the boundary between two different phases. Chemistry involving ions is ubiquitous and is of interest in the areas of atmospheric, environmental and biological sciences [1–6], as well as in the realm of engineering and technology [7,8].

Until recently, the common scientific consensus has been that ions do not exist at the air/water interface. This conventional picture, pertaining to the surface of simple salt solutions, has been based on the macroscopic experimental evidence of surface tension increase with increasing salt concentration [9]. According to the Gibbs adsorption equation, this increase in the surface tension is associated with the expulsion of ions from the air/aqueous interface [10–12]. The earliest molecular description of ions at the air/aqueous interface proposed [13,14] by Wagner, Onsager, and Samaras also predicts that surfaces are devoid of ions. Their theoretical model, which treats the interface as a sharp discontinuity between the two continuous dielectric media, and the ions as point charges, suggested that ions are repelled from the surface due to image charge repulsion. However, prompted by the need to explain chemical reactions occurring at the surface of aqueous electrolyte solutions [3,15,16], a renewed interest in understanding the air/aqueous interface of electrolyte solution has recently resurfaced.

Recent theoretical [17–20] and experimental studies [21–27] have revealed population enhancements of several inorganic anions at the aqueous interfaces. These findings have challenged the traditional notion that surfaces are devoid of ions and have

provided new insights for the ion rich interfaces. Molecular dynamic (MD) simulations using polarizable potential, which incorporates molecular interactions and electrostatic properties of ions and interfacial water molecules, showed that specific polarizable ions, e.g. I<sup>−</sup> and Br<sup>−</sup>, adsorb at the air/water surface [17–20]. Experimental evidence of these heavy halide ions and other inorganic ions, such as N<sub>3</sub><sup>−</sup>, SCN<sup>−</sup> and Fe(CN)<sub>6</sub><sup>4−</sup>, adsorbed at the air/aqueous interface has also been demonstrated by Saykally et al. [21–25] using the surface specific nonlinear spectroscopic method of second harmonic generation. Allen et al. [26] used a combination of conventional Raman spectroscopy and SFG to compare the vibrational spectra from the bulk of salt solutions with that from the surface region. Their results suggest an increased interfacial thickness of bromide and iodide solution at interfaces. Hemminger et al. [27] has directly measured the ion concentrations in the surface region of alkali halide aqueous solutions using X-ray photoelectron spectroscopy (XPS) to observe the profile of the surface composition of an alkali halide salt in contact with water vapor. Their results also support that there is a preferential enhancement of iodide and bromide ions at the water surface. Computational [28] and experimental [29] studies have also suggested that HNO<sub>3</sub> and NO<sub>3</sub><sup>−</sup> can be found at an aqueous interface with the neutral species, HNO<sub>3</sub>, being favored over the charged NO<sub>3</sub><sup>−</sup> ion.

These experimental and theoretical findings provide a new physical picture that depicts preferential adsorption of ions to the air/aqueous interface. In this description the polarizable anions preferentially adsorb to the outermost surface layer and create a highly structured surface distribution while leaving the subsequent layers of the interface devoid of anions. Consequently, integration of the entire interfacial region yields a total surface ion concentration that is depleted relative to the bulk ion concentration, and according to the Gibbs adsorption equation, an increase in the surface tension is therefore observed for these electrolyte solutions. Recently, MD simulations, along with surface tension measurements, have revealed that small organic anions also

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exhibit affinity toward the surface, which we sought to verify using the surface selective spectroscopic method of sum frequency generation.

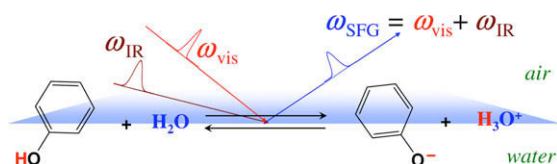
In this report, we present our studies using vibrational sum frequency generation, SFG, to investigate phenol,  $C_6H_5OH$ , and the phenolate ion,  $C_6H_5O^-$  at the air/water interface (Scheme 1). It is demonstrated that phenol, along with phenolate ion, is also present at the air/aqueous interface at high bulk pH. Phenolate ions were selected for this study chiefly because in recent work [30] it was inferred, based on surface tension measurements and molecular dynamic simulations that phenolate ions, as well as other small organic ions, exhibit a pronounced surface propensity for the air/water interface. A key assumption in the study was that at the higher bulk concentrations of sodium phenolate the decrease in surface tension is due only to the adsorption of phenolate ions. The surface excess of phenolate was then calculated with the assumption that only phenolate is at the interface; i.e. that there is no phenol at the interface.

As a complement to these experimental findings, we sought to obtain spectral evidence of phenolate ions at the air/aqueous interface for the following reasons: (1) surface tension measurements provide a macroscopic picture of an interface but does not give the molecular identity of species present at the interface, (2) in general, interfacial  $pK_a$  can and does differ from the bulk  $pK_a$ , which favors the neutral species over the charged species at the air/water interface, in which case phenol would contribute to the observed lowering of the surface tension at high pH values, (3) in determining the surface proclivity of species that exhibit acid–base chemistry it is crucial that experimental measurements are made at constant pH, because as the bulk pH changes the bulk concentration of the sodium phenolate is changed, which in turn would change the interfacial phenol–phenolate composition.

At this juncture we note the scientific importance of investigating interfacial bound phenol and phenolate ions. Phenol is a naturally occurring organic molecule that is weakly acidic with a bulk [31]  $pK_a$  of 10. Excited state deprotonation of phenol to give phenolate ion is also known to occur [32,33] for which the  $pK_a$  is 3.6. The ionized form of phenol, the phenolate anion, exhibits resonance stabilization and is electron rich, which renders it more reactive than the neutral hydroxyl form [34]. Both phenol and phenolate are pollutants, with phenolate being more reactive [34–36]. These chemical species undergo a wide range of chemical reactions that produce additional environmentally hazardous species in aqueous and gas phases [2,4].

## 2. Surface tension measurements provide macroscopic information

One very useful probe of adsorbates at planar interfaces is provided by surface tension measurements. However, surface tension is limited by the fact that it cannot differentiate the various species present at the interface, i.e. a decrease in the surface tension may imply an excess adsorption of molecular species to the surface but does not provide information as to what the species is. An important example is the air–electrolyte interface of a bulk solution containing sodium and iodide ions. Measurements showed an increase in surface tension as the concentration of NaI increased. This



Scheme 1. SFG study of acid–base reaction of phenol at the air/water interface.

increase indicates that there is a deficiency of ions at the interface [10,11], which however does not reveal whether this applies to both ions, or only one of them, and which one. Recent experimental results and molecular simulations support the claim that there is a significant population of iodide ions at the interface [22,27,37]. Similar issues apply to the presence of organic ions at aqueous interfaces because surface tension measurements do not yield the identification of surface adsorbed molecules.

## 3. Interfacial $pK_a \neq$ bulk $pK_a$

It is the surface  $pK_a$  that controls the interfacial populations of the acidic and basic forms, which favors the neutral form of the acid–base pair at the air/water interface relative to that in bulk water [38]. Second harmonic generation measurements of an insoluble long chain phenol,  $CH_3(CH_2)_{17}C_6H_4OH$  at the air/water interface yielded [38] a  $pK_a$  value of 11.7 versus a value of 10 in bulk water, which means that it is less acidic than in bulk media by a factor of 50. Similarly, studies of the insoluble long chain charged acid, hexadecylanilinium,  $CH_3(CH_2)_{15}C_6H_4NH_3^+$  at the air/water interface yielded a  $pK_a$  value of 3.6 at the interface versus 5.3 in bulk water, which is more acidic by a factor of 50 relative to that for alkyanilines in bulk water [38,39]. For both the long chain phenol surfactant and the hexadecylaniline surfactant we see that the acid–base equilibrium shifts toward the neutral form at the air/water interface, i.e. neutral phenol ionizes less at the interface than in bulk water and anilinium, which is charged, ionizes more at the interface thereby increasing the neutral form, aniline, at the interface relative to bulk water. Similar results were obtained for the insoluble long chain ammonium surfactant,  $CH_3(CH_2)_{21}NH_3^+$  at the air/water interface with the acidity increasing by a factor of 5 relative to alkyammonium acids in bulk water [40]. Neutral species were also found to be favored over charged ions in the acid–base chemistry of the carboxyl,  $-COOH$ , group at the polystyrene carboxyl particle/aqueous interface [41].

In these latter examples, it is the image charge repulsion at the air/water interface that increases the surface free energy and depending on the ion is a key factor that results in there being a deficiency in population of the charged form at the air/aqueous interface. It is because the interface  $pK_a$  is different than that in the bulk solution, and favors the neutral acid that we sought to identify and thereby differentiate the phenol and phenolate moieties at the interface using vibrational sum frequency generation. It should be noted that the  $pK_a$  of the surfactant long chain phenol–phenolate is not necessarily the same as for phenol and phenolate, which are free to leave and enter the interfacial region. Furthermore, there are constraints on the orientations of the long chain phenol, which are not present for the free phenol and phenolate species, and could thereby affect the free energies of the two species.

## 4. The importance of maintaining a constant pH

Because changes in the bulk concentration of sodium phenolate alter the bulk pH, e.g. the pH changes from 11 to 12 when the bulk concentration is increased from 0.1 M to 4 M [30]. This variation in pH leads to changes in the interfacial populations of phenol and phenolate, especially in this case because the bulk  $pK_a$  of phenol [42] is 10; consequently the surface tension measurements are affected. At low pH, i.e.  $pH < 5$ , the percent phenolate present in the solution is negligible, i.e., the ratio of phenol to phenolate is  $>10^5$ . At these pH values, it is safe to assume that the interface is overwhelmingly phenol because the bulk concentration and adsorption free energy of phenolate ions is much smaller than that of phenol. On the other hand, even at pH 12, 1% of the total bulk population is

phenol. Because phenol is much more surface active than phenolate, as shown by their very different adsorption free energies given below, its interface population is greater than 1% and therefore its contribution to the observed decrease in surface tension must be considered.

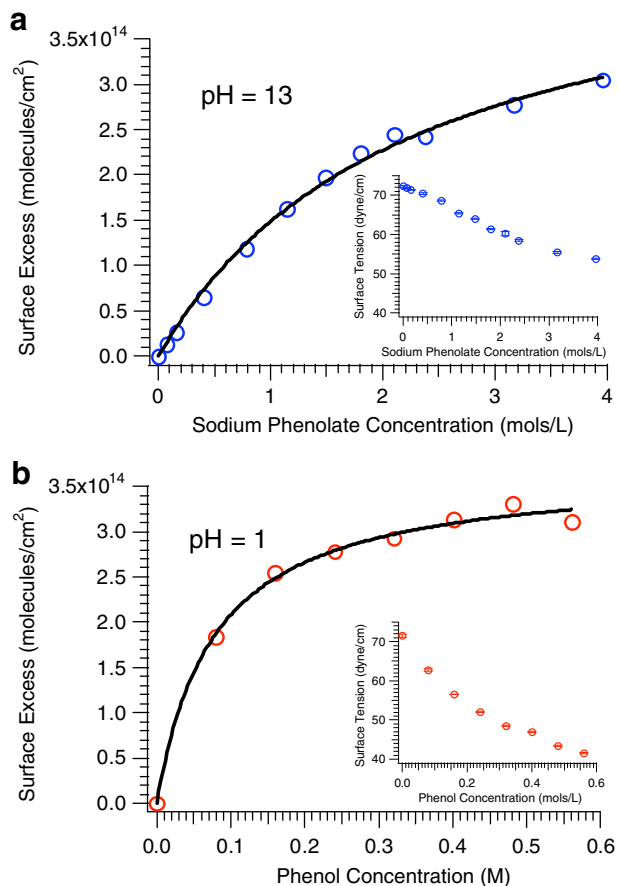
In the present investigation, the surface tension of phenol and phenolate at constant pH values of 1 and 13, were measured (Fig. 1). The purpose of selecting pH 13 was to ensure that the bulk phenolate ion concentration was greater than phenol by a factor of  $10^3$ . From the surface tension data at pH 1 and pH 13 the corresponding surface excess was calculated based on the Gibbs equation [12]. The stronger proclivity of phenol to the air/water interface [43,44] is seen in the larger adsorption equilibrium constant,  $K_{\text{ads}}^{\text{phenol}}$ , of phenol,  $682 \pm 69$ , at a bulk pH of 1, compared with phenolate  $K_{\text{ads}}^{\text{phenolate}}$  of  $24 \pm 3$  at a bulk pH of 13. Comparison of the adsorption equilibrium constants shows that phenol, being neutral, is more surface active, by a factor of 28 with respect to phenolate.

For the purpose of differentiating phenol from phenolate, sum frequency spectra were measured for the frequency range where there is a marked difference between the two species, namely the C–OH and C–O<sup>−</sup> stretches in the 1200–1300  $\text{cm}^{-1}$  region [45]. The method of vibrational SFG spectroscopy is very useful in elucidating the identity and structure of chemical species adsorbed at the air/aqueous interface and has been applied successfully to many interfaces [45–48]. The experimental SFG setup used in our measurements of the sum frequency interface spectra is described in earlier work [46]. In the experiment described here the 3 picosecond visible pulse with a bandwidth of  $\sim 11 \text{ cm}^{-1}$  and

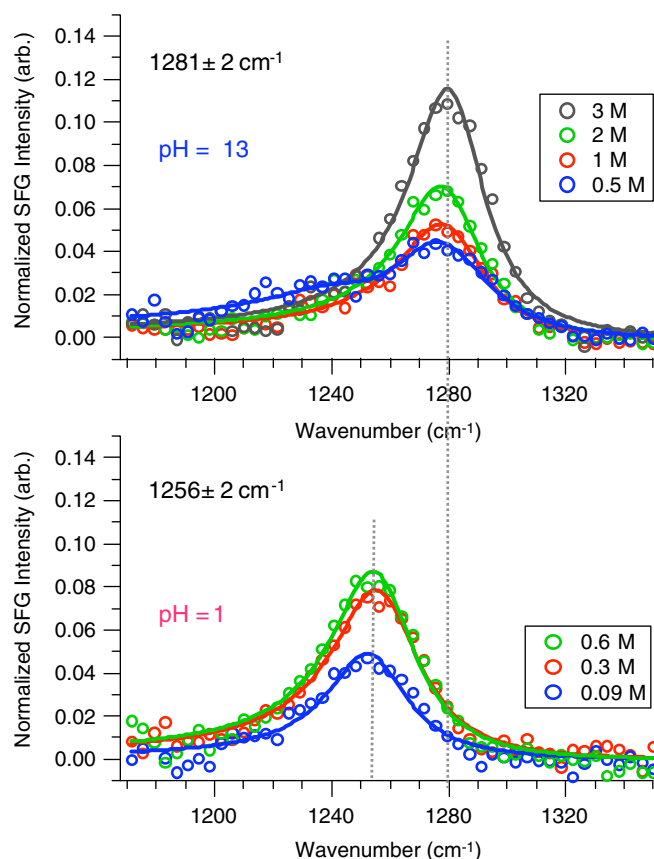
the 120 femtosecond IR beam, with a bandwidth of  $\sim 150 \text{ cm}^{-1}$ , were tuned to 800 nm and 8  $\mu\text{m}$ , respectively. The sum frequency generated, after temporal and spatial overlap of these two pulses at the sample surface, was detected using a monochromator and charged coupled device, CCD camera. The SFG intensities were normalized to a GaAs reference.

In the bulk aqueous solution the C–OH stretch of phenol and the C–O<sup>−</sup> stretch of phenolate are  $1249 \pm 2 \text{ cm}^{-1}$  for phenol and  $1281 \pm 2 \text{ cm}^{-1}$  for phenolate anion [45]. The blue shift in the carbon–oxygen stretching frequency for the phenolate anion is due to its increased force constant. When deprotonated, the C–O<sup>−</sup> bond exhibits a double bond character, which in turn shortens its bond length and increases its force constant with respect to phenol [45,47]. The concentration dependent SFG vibrational spectra of phenol and phenolate anion at the air–aqueous interface at two different pH solutions 1 and 13 are shown in Fig. 2. At bulk pH 1, a single SFG peak appears at  $1256 \pm 2 \text{ cm}^{-1}$  which is distinctly different from the maximum SFG peak at  $1281 \pm 2 \text{ cm}^{-1}$  observed for the phenolate solution at bulk pH of 13. We assign the peak at  $1281 \text{ cm}^{-1}$  to phenolate (Fig. 3), which is the same as phenolate C–O<sup>−</sup> stretch in bulk water. Similarly, the SFG peak at  $1256 \text{ cm}^{-1}$  is assigned to the interfacial phenol C–OH stretch, which is red shifted  $7 \text{ cm}^{-1}$  relative to the bulk phenol C–OH stretch. These surface spectra reveal that phenolate anions do adsorb to the air/water interface, which has been predicted from molecular dynamics simulations and correctly inferred from surface tension data [30].

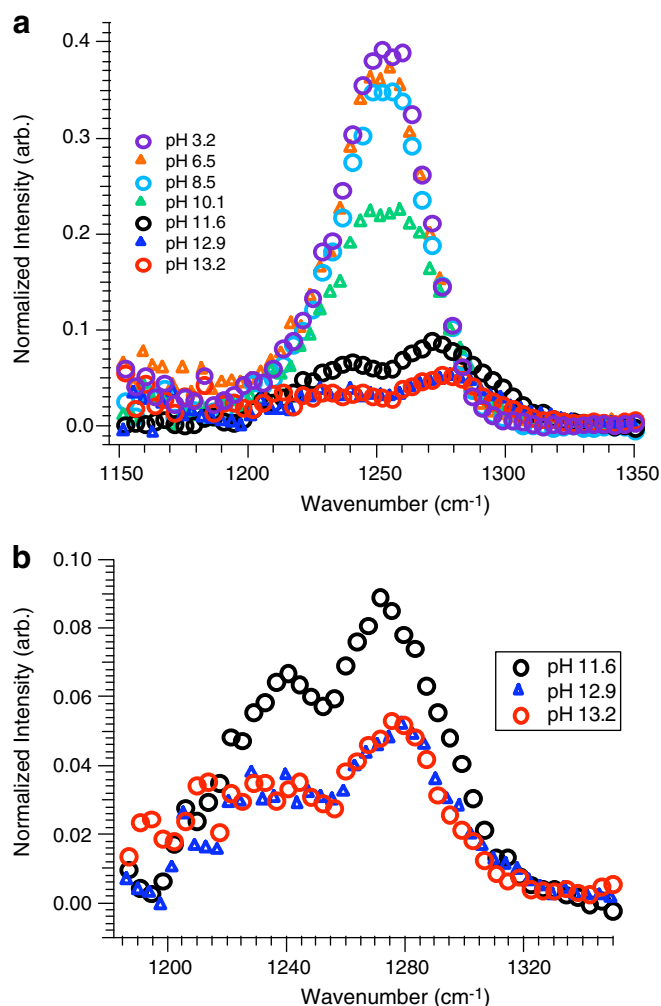
A key issue however remains and that is whether there are phenol molecules along with phenolate ions at the interface at the higher pH values. If the phenol molecules are at the interface they would contribute to the observed lowering of the air/water surface



**Fig. 1.** Surface excess of phenolate and phenol at pH 13 in (a) and pH 1 in (b) vs. bulk concentration. The insets show the measured surface tension data vs. bulk concentration. The surface excess was obtained using the Gibbs equation. The solid line is the fit to the Langmuir adsorption isotherm model.



**Fig. 2.** Normalized sum frequency surface vibrational spectra of phenolate anion (pH 13, top) and phenol (pH 1, bottom) at the aqueous–vapor interface.



**Fig. 3.** Sum frequency surface vibrational spectra of phenol/phenolate at air/water interface as a function of bulk pH. Fig. 3(a) shows vibrational SFG spectra at pH ranging from 3.2 to 13.2. Fig. 3(b) shows the spectra at pH ranging from 11.6 to 13.2.

tension. In the experimental spectra shown in Fig. 3 the concentration of phenol plus phenolate was held constant at 600 mM and a total ionic strength of 0.7 M was maintained using NaCl. It is evident that the spectral profile changes from that representing the phenol to that of the phenolate anion as the pH is increased, i.e., it shows that with increasing bulk pH, the phenol peak at  $1256\text{ cm}^{-1}$  diminishes as the peak at  $1281\text{ cm}^{-1}$ , corresponding to the phenolate anion, appears. It is apparent (Fig. 3b) that even at a bulk pH value of 11.6, which was the highest pH at which surface tension measurements were carried out [30], that there is a significant contribution from phenol to the SFG spectrum.

In conclusion, we have presented direct spectroscopic evidence that phenolate ions are adsorbed to the air/water interface using vibrational sum frequency generation. Our approach entailed probing the phenolic C–OH and C–O<sup>−</sup> vibrational stretch modes. In addition we have shown that there are phenol molecules at the air/water interface at high solution pH values [30]. Furthermore, these results demonstrate that the carbon–oxygen stretch can be used as a probe for the SFG investigation of surface bound species containing the phenolic C–OH functional group, which is abundant in many areas of chemistry.

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