

Investigation of the interfacial water structure on poly[2-(dimethylamino)ethyl methacrylate] at the air/water interface by sum frequency generation vibrational spectroscopy

WU Dan¹, GUO Yuan^{2*}, LIU GuangMing³ & ZHANG GuangZhao³

¹ Graduate University of the Chinese Academy of Sciences, Beijing 100049, China;

² Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100190, China;

³ Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

Received October 19, 2011; accepted November 13, 2011; published online February 7, 2012

The effect of pH on the conformation of surface alkyl groups and the structure of interfacial water molecules on poly[2-(dimethylamino)ethyl methacrylate] (PDEM) at the air/water interface were investigated with sum frequency generation vibrational spectroscopy (SFG-VS). At pH 4.1, the hydrogen bonding SFG spectra were similar to that of the air/pure water interface. As the pH increased from 5.4 to 9.6, the SFG intensities of both highly ordered hydrogen bonding (3200 cm⁻¹ band) and less-ordered hydrogen bonding (3400 cm⁻¹ band) were enhanced because of the charge-induced effect of deprotonated PDEM. The free OH peak disappeared completely because it was replaced by interfacial PDEM molecules. At pH 11.5, a new spectral band appeared at about 3580 cm⁻¹ in the ppp and sps spectra, and this could be assigned to the C_{2v} asymmetric stretching mode of the water molecules through molecular symmetry simulation. These hydrogen bonding structures are fully consistent with the conformational change of PDEM alkyl groups, and PDEM molecules act as a Hofmeister solvent. PDEM molecules are kosmotropic when they are charged and become more chaotropic as the pH increases.

pH, hydrogen bonding, PDEM, interface, SFG-VS

Citation: Wu D, Guo Y, Liu G M, et al. Investigation of the interfacial water structure on poly[2-(dimethylamino)ethyl methacrylate] at the air/water interface by sum frequency generation vibrational spectroscopy. *Chin Sci Bull*, 2012, 57: 984–991, doi: 10.1007/s11434-011-4963-4

Polymers have been widely studied and applied in many areas, including material science, biology, and chemical engineering [1,2]. Many of the chemical and mechanical properties of polymer materials, such as wettability, lubricity, chemical reactivity and biological compatibility, are related to the interfacial molecular structure and configuration. Therefore, it is important to understand and be able to control the molecular structures of polymers at interfaces for their application [1–3]. However, obtaining a molecular-level understanding of polymeric surfaces is challenging because it is very complicated to conduct *in situ* measurements. Sum frequency generation vibrational spectroscopy (SFG-VS) is a powerful probing technique that can be used

to investigate the structure and orientation of polymers at surfaces at the microscopic level [3,4]. Relative to other interfacial probing techniques, SFG-VS is preferred because it is nondestructive, surface selective, and monolayer sensitive [5]. SFG-VS is generally set up with a visible and a tunable infrared (IR) laser incident to the interface, and this interacts with the molecules at the interface simultaneously. The vibrational spectrum of the interfacial molecules is obtained by tuning the frequency of the IR laser and measuring the signal generated at the sum of the frequencies of visible and IR laser. SFG-VS spectra for different polarization combinations can be used to identify the surface molecular species and provide accurate information on the structure, configuration and dynamics of the interfacial molecules [5–8].

*Corresponding author (email: guoyuan@iccas.ac.cn)

In an aqueous solution, or at its surface, water-soluble polymers usually exhibit a coil-to-globule phase transition when the temperature is increased. A detailed understanding of this phase transition or thermosensitivity is required for insight into the protein folding [9]. Poly[2-(dimethylamino) ethyl methacrylate] (PDEM) is a water-soluble polymer that has notable pH-dependent thermosensitivity at the air/water interface. At the air/neutral aqueous solution interface, the thermosensitivity for PDEM is prominent, but it almost disappears at the air/acid and air/basic aqueous solution interfaces [10]. The effect of pH and temperature on PDEM molecules at the air/water interface have been investigated by Langmuir balance and SFG-VS. These studies showed that conformational change and hydration/dehydration of the PDEM chains caused this pH-dependent thermosensitivity [10].

Water is the most important chemical substance in the natural world, and the hydrogen bonding structure of liquid water plays important and complex roles in chemical and biological processes [11]. Processes such as membrane formation, protein folding, and micelle formation are often controlled by bonding interactions with water molecules at their interfaces [12]. Because the pH-dependent thermosensitivity of PDEM at its surface arise from hydration/dehydration of PDEM molecules, the environments of interfacial water molecules around PDEM chains at different pH values are quite diverse. The structures of water molecules at charged interfaces are important [2]. PDEM is a positively charged polyelectrolyte with its tertiary amine groups protonated in acidic and neutral aqueous solutions [13], and its hydrophilic groups can hydrogen bond with adjacent water molecules at the air/water interface. Consequently, interfacial water molecules around PDEM should become more ordered as the pH of the aqueous solution is changed and the surface charge increases [14]. While the pH-dependent conformational change of PDEM molecules at the air/water interface has been determined using SFG-VS [10], the structure and bonding of interfacial water molecules remains unclear. In the present study, we investigated the effect of pH on the interfacial hydrogen bonding on a PDEM monolayer adsorbed at the air/water interface. These results can be used to understand the interfacial interactions that occur between the water molecules and polymers.

1 Basic theory of SFG-VS

The SFG intensity reflected from an interface can be expressed as a square function of the effective second-order susceptibility $\chi_{\text{eff}}^{(2)}$ as follows [15]:

$$I(\omega) = \frac{8\pi^3 \omega^2 \sec^2 \beta}{c^3 n_1(\omega) n_1(\omega_1) n_1(\omega_2)} \left| \chi_{\text{eff}}^{(2)} \right|^2 I(\omega_1) I(\omega_2), \quad (1)$$

where ω , ω_1 and ω_2 are the frequencies of the SFG signal,

visible, and IR laser beams, respectively; $n_j(\omega_j)$ is the refractive index of bulk medium, j , at frequency ω_j , β is the angle from the interface normal of the SFG signal, and $I(\omega_j)$ is the intensity of the SFG signal or the input laser beams.

Because $\chi_{\text{eff}}^{(2)}$ depends on the infrared frequency, ω_2 , the following equation applies:

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR,eff}}^{(2)} + \sum_q \frac{\chi_{q,\text{eff}}^{(2)}}{\omega_2 - \omega_q + i\Gamma_q}, \quad (2)$$

where $\chi_{\text{NR,eff}}^{(2)}$ is the non-resonant contribution, and $\chi_{q,\text{eff}}^{(2)}$ is the susceptibility strength factor for the q th vibrational mode in the SFG spectra centered at the vibrational frequency, ω_q , with a damping constant Γ_q . Because there is more than one vibrational mode ($q > 1$), the observed SFG-VS spectra are subject to interference from different vibrational modes. The effect of interference can be understood by fitting the observed SFG spectra with multiple modes following eq. (2). The relative values and signs of the $\chi_{\text{NR,eff}}^{(2)}$ and $\chi_{q,\text{eff}}^{(2)}$ factors, and the spectral parameters ω_q and Γ_q , can be determined from this spectral fitting [16].

At a rotationally isotropic interface ($C_{\infty v}$), $\chi_{\text{eff}}^{(2)}$ is related to the seven nonzero macroscopic susceptibility tensors $\chi_{ijk}^{(2)}$, and can be expressed as the following four independent experimentally measurable terms [8]:

$$\begin{aligned} \chi_{\text{eff,ssp}}^{(2)} &= L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)\sin\beta_2\chi_{yyz}^{(2)}, \\ \chi_{\text{eff,sps}}^{(2)} &= L_{yy}(\omega)L_{zz}(\omega_1)L_{yy}(\omega_2)\sin\beta_1\chi_{yyz}^{(2)}, \\ \chi_{\text{eff,pss}}^{(2)} &= L_{zz}(\omega)L_{yy}(\omega_1)L_{yy}(\omega_2)\sin\beta\chi_{zyy}^{(2)}, \\ \chi_{\text{eff,ppp}}^{(2)} &= -L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2\chi_{xxz}^{(2)} \\ &\quad - L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2\chi_{xxz}^{(2)} \\ &\quad + L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2\chi_{zzx}^{(2)} \\ &\quad + L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2\chi_{zzz}^{(2)}. \end{aligned} \quad (3)$$

The xy plane in the laboratory coordinate system $\lambda(x, y, z)$ is defined as the plane of the interface, with z as the interface normal; $L_{ii}(i = x, y, z)$ is the Fresnel coefficient, which is determined by many factors [8,15]. The $\chi_{ijk}^{(2)}$ tensors are related to the molecular hyperpolarizability tensor $\beta_{ij'k'}^{(2)}$ in the molecular coordinate system $\lambda'(a, b, c)$ through the summed average over all molecular orientations, which can be described as follows [8,15]:

$$\chi_{ijk}^{(2)} = N_s \sum_{i'j'k'} \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta_{ij'k'}^{(2)}, \quad (4)$$

where N_s is the number density of the interface moiety under investigation, and $R_{\lambda\lambda'}$ is a parameter for the Euler rotational transformation matrix from the molecular coordinate system $\lambda'(a, b, c)$ to the laboratory coordinate system $\lambda(x, y, z)$.

z). The expressions of the relationship between the $\chi_{ijk}^{(2)}$ tensors and $\beta_{ijk}^{(2)}$ tensors for the molecular groups with C_{2v} , C_{3v} and $C_{\infty v}$ symmetry have been described in the literature [8,17–19]. Thus, molecular groups investigated in SFG-VS, such as CH_3^- , $-\text{CH}_2^-$, CH , $-\text{CO}$, $-\text{CN}$ and $-\text{OH}$ groups, can be easily treated.

Polarization dependence analysis was based on eq. (3), and symmetry analysis was based on eq. (4) [8], these formulas and methods form the basis of the quantitative analysis in SFG-VS.

2 Experimental

Hydrochloric acid (37% in water, purity 98%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) or sodium hydroxide pellets (purity 99.99%, Sigma-Aldrich, St. Louis, MO) in ultrapure deionized water (18.2 M Ω cm, from standard Millipore treatment) was used to control the pH of the aqueous solution. The pH of the solution was measured using a Mettler-Toledo (Columbus, OH) pH meter with a precision of ± 0.01 . The structure of the PDEM homopolymer is shown in Figure 1. A solution of PDEM (0.1 mg mL $^{-1}$) in chloroform (20 μL) was spread on an air/water interface in a round teflon dish ($\phi 4.5$ cm) using a mini syringe. After complete evaporation of chloroform (20–30 min), a PDEM monolayer formed on the water surface, and this was used for SFG-VS measurement.

The experimental setup has been described previously [18,19]. Briefly, a 10 Hz and 23 ps SFG spectrometer laser system from EKSPLA (Vilnius, Lithuania) was set in a co-propagating configuration. The visible wavelength was fixed at 532.1 nm and the full range of the IR tunability was from 1000 to 4300 cm^{-1} . The specified spectral resolution of this SFG spectrometer is < 6 cm^{-1} in the IR range, and about 2 cm^{-1} at around 3000 cm^{-1} . In the experiment (3000–3800 cm^{-1}), the incident angles were 63° and 50° for the visible and the IR laser beams, respectively. Each spectrum was scanned with 5 cm^{-1} steps and averaged over 600 laser pulses. The SFG spectra were normalized over the incident IR and visible energies and then normalized with the SFG

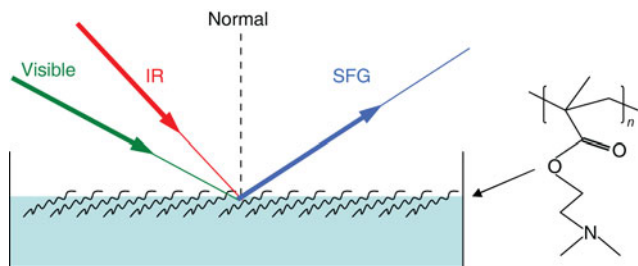


Figure 1 The experimental setup for SFG-VS of the air/water interface for adsorbed PDEM.

spectra of a thick z-cut quartz crystal [16]. The energy of the visible beam was typically less than 300 μJ and that of the IR beam less than 200 μJ . There was no evidence of a heating effect or photoinduced reactions under these experimental conditions. All measurements were carried out at a controlled temperature ($22.0 \pm 0.5^\circ\text{C}$) and humidity ($40\% \pm 10\%$). The whole experimental setup on the optical table was covered in a plastic housing to reduce air flow.

3 Results and discussion

3.1 Conformational change of PDEM molecules

Figure 2 shows the effect of the pH on conformational changes of the PDEM homopolymer adsorbed at the clean

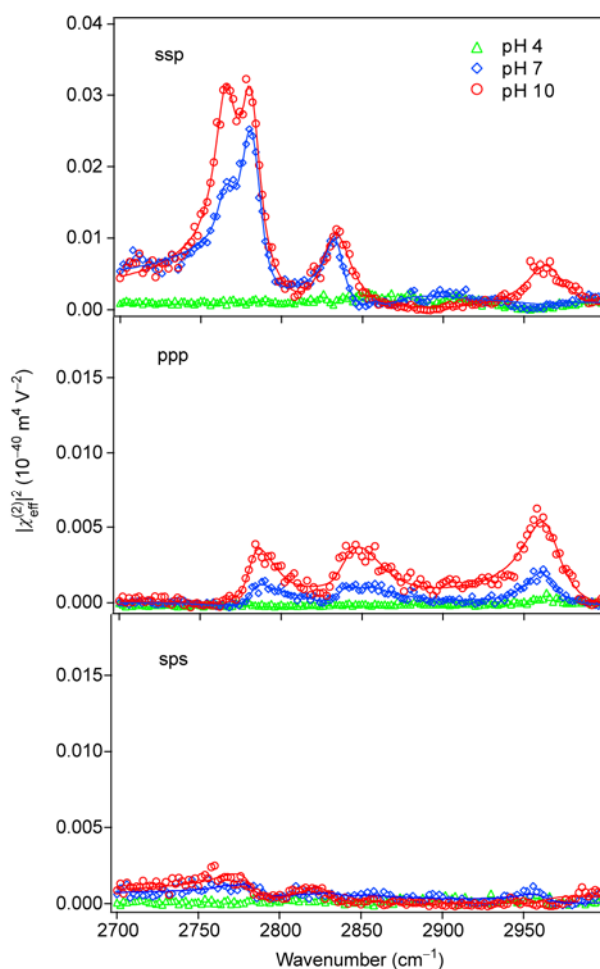


Figure 2 SFG-VS spectra of the PDEM homopolymer at the air/aqueous solution interface in the ssp, ppp and sps polarization combinations at three pH values. Here ssp denotes the polarization combinations of the SFG signal field (s polarization), the incident visible field (s polarization) and the incident IR field (p polarization). The symbol p means that the optical field vector is within the incident plane in the experimental configuration, and s means that the field vector is perpendicular to this incident plane. The solid lines are the fitted curves with the Lorentzian line shape function in eq. (2).

air/aqueous solution interface, we have published these results previously [10]. The SFG-VS spectra presented in Figure 2 were fit with the results in Table 1. Briefly, at pH 4, the tertiary amine groups of PDEM are fully charged [13] and PDEM is so hydrophilic that almost the whole PDEM chain is pulled into the water phase. Therefore, no alkyl group can be detected by SFG-VS in any polarization combination at the surface.

At pH 7, the amine groups are partially charged [13]. With accompanying dehydration of the PDEM chains, the amine groups partially protrude into the air. Both the amine methyl and methylene groups are present at the air/water interface, but the methylene group orients with a large angle from the surface normal because of its weak SFG intensity in the ssp spectrum. Three C–H bands are clearly observed at about 2766, 2782 and 2834 cm^{-1} in the ssp polarization combination, and these can be attributed to the methylene symmetric stretching vibration ($-\text{N}-\text{CH}_2-\text{ss}$), methyl symmetric stretching vibration ($-\text{N}-\text{CH}_3-\text{ss}$), and methyl symmetric stretching Fermi resonance ($-\text{N}-\text{CH}_3-\text{ss}-\text{Fermi}$), respectively. In the ppp spectrum, the bands at about 2782 and 2834 cm^{-1} belong to the methyl symmetric stretching vibrational mode ($-\text{N}-\text{CH}_3-\text{ss}$) and methyl symmetric stretching Fermi resonance ($-\text{NCH}_3-\text{ss}-\text{Fermi}$), respectively. The 2961 cm^{-1} peak can be assigned to the methyl asymmetric stretching vibrational mode ($-\text{NCH}_3-\text{as}$) [10,18–21].

Finally, at pH 10, the amine groups are uncharged and hydrophobic [13]. In this state, they completely protrude into the air phase, and the air/water interface is covered with more amine groups than that at pH 7. Moreover, the orientations of the amine methyl and methylene groups are more perpendicular relative to the surface plane than at pH 7. As a result, the SFG intensities of all six peaks in the ssp and ppp polarization combinations are enhanced, and new peaks appear at 2845 cm^{-1} in ppp spectrum and 2964 cm^{-1} in the ssp spectrum. The 2845 cm^{-1} peak arises from the methylene asymmetric stretching vibrational mode ($-\text{N}-\text{CH}_2-\text{as}$), and the 2964 cm^{-1} peak is mainly from the methylene

symmetric stretching Fermi resonance mode ($\text{N}-\text{CH}_2-\text{ss}-\text{Fermi}$) with a small contribution from methyl asymmetric stretching vibration mode ($\text{N}-\text{CH}_3-\text{as}$) [18,19]. In Table 1, the χ_q values of the 2766 and 2782 cm^{-1} peaks have opposite signs, which indicates that the amine methyl groups protrude into the air phase and the amine methylene groups extend into the aqueous solution. Therefore, the lone electron pair of the nitrogen atom should point down toward the water phase. Additionally, the absence of the SFG signal from the main chain at any pH value can be explained by the orientation of almost all of the segments in the main chain below or parallel to the air/water interface.

3.2 Bonding and structure of the interfacial water molecules

Figure 3 gives the SFG-VS spectra at the air/pure water interface in the OH stretching region. These results fully agree with those reported previously [16,22]. In the ssp polarization combination, the main features are a very broad band (3000–3500 cm^{-1}) and a sharp peak (approximately 3700 cm^{-1}). The broad band is composed of two broad peaks, centered at about 3200 and 3400 cm^{-1} . The former can be attributed to ordered hydrogen bonded OH, as in the tetrahedrally coordinated structure of the water molecules in the bulk ice (ice-like hydrogen bonding), and the latter can be assigned to less ordered hydrogen bonding, as in the bulk water (liquid-like hydrogen bonding). The sharp peak at 3700 cm^{-1} is associated with the dangling OH, which protrudes out of the air/water interface. The water molecules contributing to this peak must be located at the top monolayer of the surface. Moreover, the 3200 and 3400 cm^{-1} bands belong to the symmetric stretching vibrational modes with C_{2v} symmetry of the water molecules, and the free OH peak has $C_{\infty v}$ symmetry. In the ppp spectrum, a band at 3500 cm^{-1} can be attributed to the other OH bond from the water molecule with the free OH. This also has $C_{\infty v}$ symmetry and is hydrogen-bonded with the adjacent water

Table 1 Fitting results of the SFG-VS spectra in Figure 2^{a)}

pH 10	ω_q (cm^{-1})		2766.1±0.3	2781.6±0.5	2833.4±0.5	2844.8±3.1	2964.4±0.7
	Γ_q (cm^{-1})	χ_{NR}	11.6±0.5	8.3±0.5	12.2±0.6	28.1±2.4	14.7±0.8
	ssp	−0.027±0.001	−1.849±0.108	1.506±0.199	1.159±0.170	−0.081±0.414	1.109±0.056
	ppp	−0.016±0.002	−0.277±0.122	−0.577±0.063	−0.205±0.111	1.678±0.194	1.000±0.055
	sps	−0.080±0.072	−0.110±0.191	0.064±0.061	0.141±0.136	−1.005±0.197	−0.035±0.039
	pH 7	ω_q (cm^{-1})		2765.7±0.3	2782.7±0.3	2834.0±0.4	2857.2±1.4
Γ_q (cm^{-1})		χ_{NR}	9.4±0.9	8.4±0.2	6.6±0.6	10.8±1.7	11.1±1.9
ssp		−0.034±0.002	−1.003±0.115	1.153±0.035	0.395±0.049	−0.266±0.105	−0.256±0.227
ppp		−0.010±0.003	−0.090±0.154	−0.298±0.041	−0.156±0.040	0.091±0.067	0.435±0.068
sps		−0.022±0.006	−0.164±0.116	−0.128±0.037	0.021±0.037	0.043±0.087	0.159±0.058

a) The peak position, ω_q , damping constant, Γ_q , sum-frequency susceptibility strength factor, χ_q and non-resonant term, χ_{NR} , are listed in the table. The units of both χ_q and χ_{NR} are $10^{-20} \text{ m}^2 \text{ V}^{-1}$.

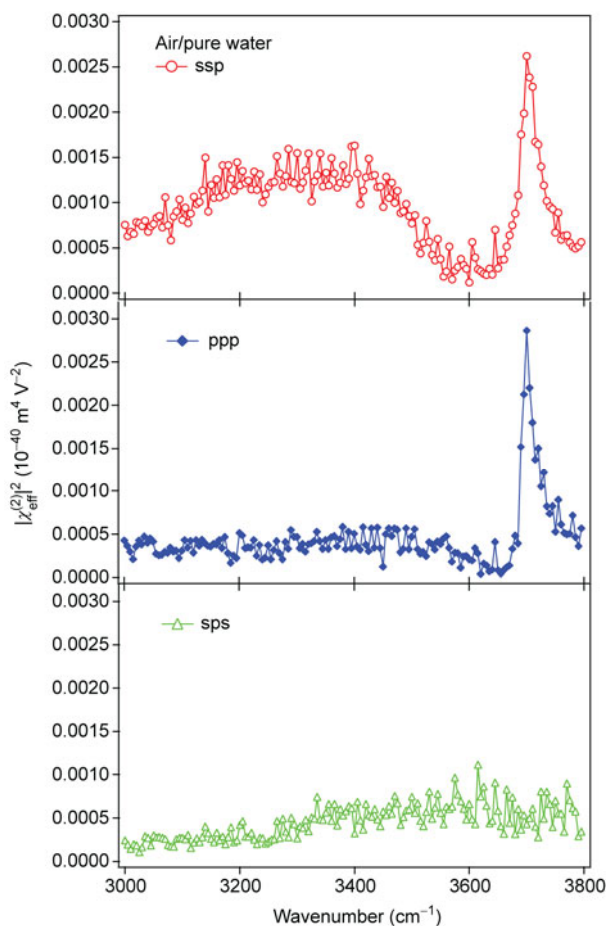


Figure 3 SFG-VS spectra at the vapor/pure water interface in the 3000–3800 cm^{-1} region under the polarization combinations ssp, ppp and sps. The solid lines join consecutive data points as a visual guide.

molecules [16].

Because the tertiary amine groups of PDEM can be protonated in acidic and neutral aqueous solutions, while the PDEM homopolymer can adsorb at the air/aqueous solution interface at different pH values, the percentage of charged PDEM molecules at the surface can be calculated using the following equation [13]:

$$\text{p}K_{\text{as}} = \log \frac{n_s}{n - n_s} + \text{pH}, \quad (5)$$

where $\text{p}K_{\text{as}}$ is the surface $\text{p}K_{\text{a}}$ of the polyelectrolyte molecule, n_s is the number of charged molecules, and n denotes the total number of molecules. The $\text{p}K_{\text{as}}$ of PDEM is 6.7 ± 0.2 [13], and the percentages of charged molecules (n_s/n) at different pH values for this $\text{p}K_{\text{as}}$ are listed in Table 2. When the pH increased, the percentage of charged molecules

Table 2 Percentage of charged PDEM molecules at different pH values

pH	4.1	5.4	7.0	9.6	11.5
n_s/n (%)	99.8	95.2	33.3	0.12	0.00

decreased. This led to gradual neutralization of the PDEM molecule and a reduction of its water solubility, which led to pH dependent conformational change of the PDEM polymers at the air/water interface [10].

The hydrogen bonding structure of the interfacial water molecules on PDEM monolayer adsorption at the clean air/water interface was measured by SFG-VS, and the corresponding spectra are shown in Figure 4. The pH dependence of the hydrogen bonding strength can be observed in these spectra. At pH 4.1, the magnitude and peak position of the broad band in the 3100–3500 cm^{-1} region and the free OH peak in both the ssp and ppp polarization combinations are basically the same as that of the air/pure water interface. This means that the amount and structure of the interfacial water molecules remains almost unchanged, and all of the PDEM polymers should not be at the surface and should have no influence on the surface water molecules. From Table 2, the percentage of charged PDEM polymer is 99.8%. These results are consistent with the conclusion that the PDEM molecules were fully charged and completely

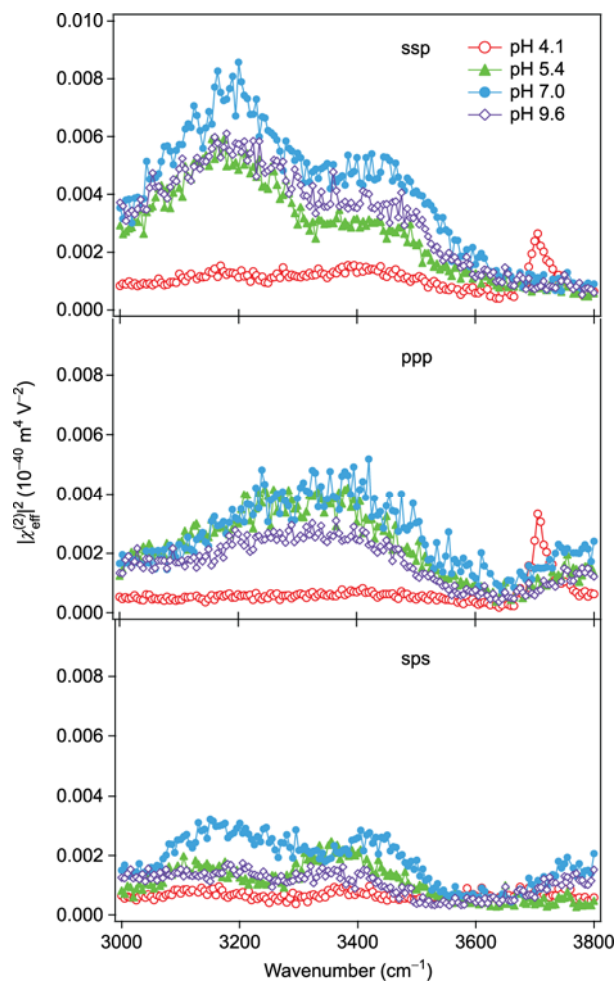


Figure 4 SFG-VS spectra of the interfacial water molecules on PDEM adsorption at the air/water interface in the ssp and ppp polarization combinations. The solid lines join consecutive data points as a visual guide.

entered into the bulk water phase at pH 4.

At pH 5.4, in the ssp spectrum, the SFG intensities of the highly ordered hydrogen bonding band (3200 cm^{-1}) and less-ordered hydrogen bonding band (3400 cm^{-1}) increased, while the 3700 cm^{-1} peak disappeared completely. These spectral phenomena indicate that the interfacial water molecules are more ordered, and the free OH are replaced by the PDEM molecules. At this pH, the percentage of charged PDEM polymer is 95.4%, and although most of the polymers are located in the bulk water, some have emerged onto the air/water interface.

As the pH increased to 7.0, the magnitude of the 3200 cm^{-1} and 3400 cm^{-1} hydrogen bonds increased to about 5–6 and 3–4 times what they were at the air/pure water interface (Figure 3), respectively. The 3700 cm^{-1} peak disappeared completely. Because PDEM is partially charged (33.3%), most of the PDEM molecules are present at the air/water interface. This is also apparent from the C-H stretching SFG-VS spectra in Figure 2. Therefore, the charge at the surface, which is determined by the amount of PDEM at the surface and the percentage charge percent of the PDEM, is greater than that at pH 4.1. As a result of the charge-induced effect [12,23,24], the water molecules are more ordered, and the thickness of ordered water molecules increases, which strengthens the hydrogen bonding. The positively charged amine group lies on the kosmotropic side of the Hofmeister cation series [25], and PDEM molecules act as a Hofmeister solvent. They are kosmotropic when charged and become more chaotropic as the pH increases. This results in increasing SFG intensity of the interfacial water as the pH increases from 4.1 to 7.0 [26,27].

Finally, at pH 9.6, the highly ordered and less-ordered hydrogen bond strengths decrease relative to those that at pH 7.0. This can be easily understood by considering the OH^- concentration is higher than the concentration of the amine group, and OH^- dominates the interfacial species, which decreases the SFG intensity. The interfacial water molecules also decrease as the polymers adsorb at the surface (Figure 2).

Apparently, the 3200 cm^{-1} band is much stronger than the 3400 cm^{-1} band at all pH values. This is because the effect of the electronic field is larger on the highly ordered hydrogen bond than on the less-ordered hydrogen bond. Furthermore, both of the hydrogen bonding bands can be attributed to the C_{2v} symmetric stretching vibrational mode of the OH bonds from interfacial water molecules [16]. In the ppp spectra, the free OH peak disappears when the pH is increased from 5.4 to 9.6, and a new broad band ($3100\text{--}3500\text{ cm}^{-1}$) centered at about 3350 cm^{-1} appears. According to the polarization selection rules [8,16], this band cannot be assigned to the C_{2v} or $C_{\infty v}$ symmetry of the water molecules. It may arise from other water species with some certain symmetry. This interesting spectral phenomenon needs to be investigated further.

3.3 New spectral features and molecular symmetry simulation

Figure 5 shows the SFG-VS spectra of the interfacial water molecules in the $3000\text{--}3800\text{ cm}^{-1}$ region at pH 11.5. At this pH, the PDEM molecule is totally deprotonated and uncharged, which means it is insoluble in the bulk aqueous solution and preferentially stays at the air/water interface. Its hydrophobic groups, such as $-\text{NCH}_2$ and $-\text{N}-\text{CH}_3$, protrude into the air phase, and it has no associated water molecules. No charge-induced effect exists and the amount of surface water molecules is reduced to the minimum. Therefore, in the ssp spectrum, the magnitudes of both the 3200 and 3400 cm^{-1} bands decrease considerably. However, because the interfacial water molecules hydrate the ester groups of the PDEM molecules with a preferred orientation [28], they contribute to the SFG intensity of the 3200 cm^{-1} and 3400 cm^{-1} bands through strong hydrogen bonding of water coupled to the hydrophilic groups. Consequently, the hydrogen bonding strength of the ordered hydrating water is similar to that of the air/pure water interface.

The most striking feature in the spectra is that a new broad band appears at about 3580 cm^{-1} in both the ppp and sps polarization combinations, but in the ssp spectrum the SFG intensity is much lower and no obvious peak can be observed. Similar spectral phenomena were reported by Tyrode et al. [28,29], where experiments were conducted on a nonionic surfactant monolayer adsorbed at an air/water interface. The difference in our spectra is that the magnitude of this peak is bigger than that of the free OH peak. In the report by Tyrode et al. [28,29], the peak intensity was about half of that of the free OH peak, and this can be explained by the different structure and amount of these water molecules. They concluded that this band came from the non-hydrogen bonded water species with both OH bonds protruding into the air phase close to the surfactant hydrocarbon tails. However, Richmond et al. [30] suggested this band

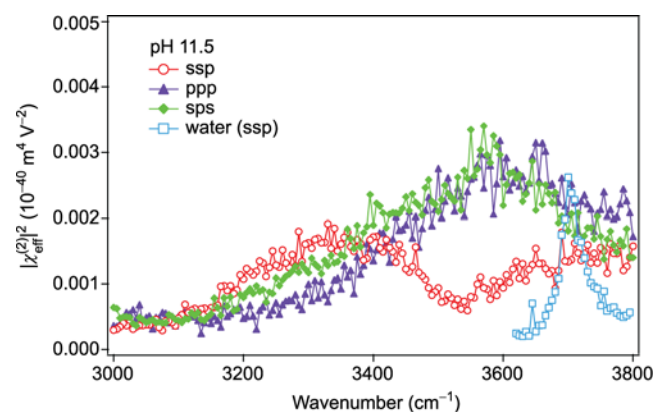


Figure 5 Hydrogen bonding SFG-VS spectra on PDEM adsorption at the air/water interface at pH 11.5. The free OH peak of the ssp spectra at the air/pure water interface in Figure 3 is shown for comparison. The solid lines join consecutive data points as a visual guide.

was from weak hydrogen bonding between the water molecules and the head groups of phospholipid monolayer at the air/water interface.

Using the orientational function of SFG-VS reported in our previous paper [8], the general orientational parameter, c , and the strength factor, d , can be calculated with $C_{\infty v}$ and C_{2v} symmetry of the water molecules (Table 3). The parameters of the air/water interface are the same as those used by Wang [8], Wei [22] and Hirose [31] et al.; which were $n_1(\omega) = n_1(\omega_1) = n_1(\omega_2) = 1$, $n_2(\omega) = n_2(\omega_1) = 1.34$, $n_2(\omega_2) = 1.18$, $n'(\omega) = n'(\omega_1) = 1.15$, $n'(\omega_2) = 1.09$. As we have demonstrated previously [18,19,32], the plot of $[dr(\theta)]^2$ against the orientation angle θ with the distribution $\sigma=0$ in different polarizations can be used for polarization analysis of SFG-VS data. Using the parameters in Table 3, we plotted the SFG intensities against θ in Figure 6. From Figure 5, we can see the magnitudes of the 3580 cm^{-1} peaks in the ppp and sps spectra are almost the same, and a little stronger than that of the free OH peak at the air/water interface. However, in the ssp spectrum a pronounced minimum is observed instead. Obviously, the SFG intensity relationship at 3580 cm^{-1} in the ssp, ppp and sps spectra fits well with the simulation of the C_{2v} symmetry asymmetric stretching mode in Figure 6, and cannot belong to the C_{2v} or $C_{\infty v}$ symmetry symmetric stretching modes. Moreover, the intensity ratio between the ppp and sps polarization combinations for this band is close to 1. For a ratio like this, the obtained orientation angles range from 30° to 40° from the surface normal. These numbers are a rough estimate as the δ distribution of angles was assumed in the calculation, which implies that all of the water molecules responsible for this band have exactly the same orientation and this is inconsistent with the broad nature of

the “non-hydrogen bonded” band. A more realistic Gaussian function for the distribution of the orientation angle was also evaluated, and showed very similar trends (data not shown). These results agree with the earlier conclusion [28,29].

Because the spectral feature from water molecules with the asymmetric stretching mode of C_{2v} symmetry was not observed in the SFG spectra of the air/pure water interface [16,17,33], the interpretation of weak hydrogen bonding between the water molecules and the hydrophilic groups of PDEM molecules for the 3580 cm^{-1} band may be unreasonable. Therefore, this band can be attributed to the non-hydrogen bonded water molecules with both hydrogen atoms approaching the hydrophobic alkyl chains of the PDEM molecules out of the liquid phase. Consequently, they do not participate in hydrogen bonds with other water molecules in the bulk phase.

When the pH is 11.5, there is no charge at the air/water interface and the hydration effect with the hydrophilic groups of PDEM polymers is the main factor enhancing the hydrogen bonding in Figure 5. This hydration effect is apparently much more influential on the less-ordered hydrogen bonding than on the highly ordered hydrogen bonding, which increases the intensity of the 3400 cm^{-1} band relative to the 3200 cm^{-1} band. For the ssp spectra (Figure 4), at pH 4.1–9.6, the 3200 cm^{-1} band is stronger than the 3400 cm^{-1} band. Therefore, we can conclude that the charge-induced effect has more influence on the highly ordered hydrogen bonding than that on the less-ordered hydrogen bonding. Compared to the hydration effect, the charge-induced effect enhances the hydrogen bonding more. Therefore, the intensity of hydrogen bonding at pH 11.5 is much weaker than that at pH 4.1–9.6.

Table 3 The general orientational parameter, c , and strength factor, d , for $C_{\infty v}$ symmetry, symmetric stretching (ss) and asymmetric stretching (as) modes with C_{2v} symmetry of the water molecules in different polarization combinations^{a)}

Symmetry	d (ssp)	c (ssp)	d (ppp)	c (ppp)	d (sps)	c (sps)
$C_{\infty v}$	0.17	0.52	-0.038	5.8	0.11	1
C_{2v} -ss	0.19	0.038	-0.044	-0.42	0.092	1
C_{2v} -as	-0.076	1	0.19	1.0	0.00019	-500

a) The d value of $C_{\infty v}$ symmetry has the unit β_{cc} of a single OH bond, and the d values of C_{2v} symmetry are absolute values.

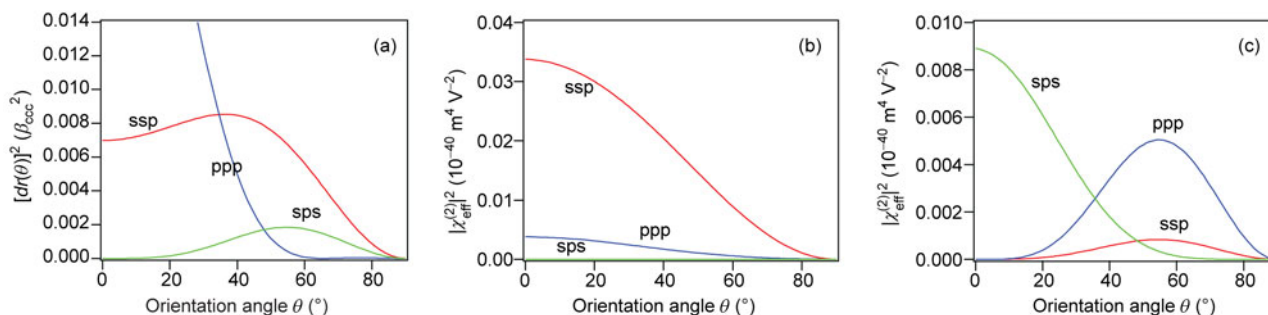


Figure 6 The simulated SFG intensities for $C_{\infty v}$ symmetry (a), C_{2v} symmetry symmetric stretching (ss) mode (b) and asymmetric stretching (as) mode (c) of water molecules at different orientation angles θ assuming $\sigma=0$. The $[dr(\theta)]^2$ has the unit β_{cc}^2 of a single OH bond.

4 Conclusions

In this paper, the pH-dependent hydrogen bonding structure of PDEM homopolymer adsorbed at the air/water interface was systematically investigated using SFG-VS based on conformational changes of the PDEM molecules. When the PDEM molecules were charged, the electronic field-induced effect determined the hydrogen bonding intensity of interfacial water. Furthermore, the SFG intensity change of the interfacial water originated from the change of the kosmotropic properties of the amine moieties. This provides molecular-level insight into the interfacial water structure. The influence of the charge-induced effect on the highly-ordered hydrogen bonding was greater than that on the less-ordered hydrogen bonding. Additionally, the asymmetric stretching mode of C_{2v} symmetry of the interfacial water molecules was observed and confirmed through molecular symmetry simulation for the water molecule. These approaches and conclusions provide direction for studies of charged and uncharged interfaces, including polymers and other complex molecules, and provide insight on chemical and biological problems related to water molecules.

Thanks Prof. Hong-fei Wang and Cheng-cheng Ma for discussions and guidance. This work was supported by the Main Direction Program of Knowledge Innovation of Chinese Academy of Sciences (KJ CX-EW-W09) and the National Natural Science Foundation of China (91027042, 21073199).

- Feast W J, Munro H S, Richards R W. *Polymer Surface and Interface II*. New York: John Wiley and Sons, 1992
- Garbassi F, Morra M, Occhiello E. *Polymer Surface, from Physics to Technology*. New York: John Wiley and Sons, 1994
- Chen Z, Shen Y R, Somorjai G A. Studies of polymer surfaces by sum frequency generation vibrational spectroscopy. *Annu Rev Phys Chem*, 2002, 53: 437–465
- Gracias D H, Chen Z, Shen Y R, et al. Molecular characterization of polymer and polymer blend surfaces. Combined sum frequency generation surface vibrational spectroscopy and scanning force microscopy studies. *Acc Chem Res*, 1999, 32: 930–940
- Miranda P B, Shen Y R. Liquid Interfaces: A study by sum-frequency vibrational spectroscopy. *J Phys Chem B*, 1999, 103: 3292–3307
- Shen Y R. Surface properties probed by second-harmonic and sum-frequency generation. *Nature*, 1989, 337: 519–525
- Bain C D. Sum-frequency vibrational spectroscopy of the solid/liquid interface. *J Chem Soc Faraday Trans*, 1995, 91: 1281–1296
- Wang H F, Gan W, Lu R, et al. Quantitative spectral and orientational analysis in surface sum frequency generation vibrational spectroscopy (SFG-VS). *Int Rev Phys Chem*, 2005, 24: 191–256
- Creighton T E. *Protein Folding*. New York: Freeman, 1992
- Liu G M, Wu D, Ma C C, et al. Insight into the origin of the thermosensitivity of poly[2-(dimethylamino)ethyl methacrylate]. *Chem Phys Chem*, 2007, 8: 2254–2259
- Garrett B C. Ions at the air/water interface. *Science*, 2004, 303: 1146–1147
- Richmond G L. Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chem Rev*, 2002, 102: 2693–2724
- An S W, Thomas R K. Determination of surface pK_a by the combination of neutron reflection and surface tension measurements. *Langmuir*, 1997, 13: 6881–6883
- Kim J, Cremer P S. IR-visible SFG investigations of interfacial water structure upon polyelectrolyte adsorption at the solid/liquid interface. *J Am Chem Soc*, 2000, 122: 12371–12372
- Zhuang X, Miranda P B, Kim D, et al. Mapping molecular orientation and conformation at interfaces by surface nonlinear optics. *Phys Rev B*, 1999, 59: 12632–12640
- Gan W, Wu D, Zhang Z, et al. Polarization and experimental configuration analyses of sum frequency generation vibrational spectra, structure, and orientational motion of the air/water interface. *J Chem Phys*, 2006, 124: 114705
- Du Q, Freysz E, Shen Y R. Vibrational spectra of water molecules at quartz/water interfaces. *Phys Rev Lett*, 1994, 72: 238–241
- Lu R, Gan W, Wu B H, et al. Vibrational polarization spectroscopy of CH stretching modes of the methylene group at the vapor/liquid interfaces with sum frequency generation. *J Phys Chem B*, 2004, 108: 7297–7306
- Lu R, Gan W, Wu B H, et al. C-H stretching vibrations of methyl, methylene and methine groups at the vapor/alcohol ($n = 1-8$) interfaces. *J Phys Chem B*, 2005, 109: 14118–14129
- Bellamy L J. *The Infrared Spectra of Complex Molecules*. London: Chapman and Hall, 1975
- Bower D I, Maddams W F. *The Vibrational Spectroscopy of Polymers*. Cambridge: Cambridge University Press, 1989
- Wei X, Shen Y R. Motional effect in surface sum-frequency vibrational spectroscopy. *Phys Rev Lett*, 2001, 86: 4782–4799
- Gragson D E, McCarty B M, Richmond G L. Ordering of interfacial water molecules at the charged air/water interface observed by vibrational sum frequency generation. *J Am Chem Soc*, 1997, 119: 6144–6152
- Shultz M J, Schnitzer C, Baldelli S. Sum frequency generation spectroscopy of the aqueous interface: Ionic and soluble molecular solutions. *Int Rev Phys Chem*, 2000, 19: 123–153
- Cacace M G, Landau E M, Ramsden J J. The Hofmeister series: Salt and solvent effects on interfacial phenomena. *Quart Rev Biophys*, 1997, 30: 241–277
- Gurau M C, Lim S M, Castellana E T, et al. On the mechanism of the Hofmeister effect. *J Am Chem Soc*, 2004, 126: 10522–10523
- Chen X, Yang T L, Kataoka S, et al. Specific ion effects on interfacial water structure near macromolecules. *J Am Chem Soc*, 2007, 129: 12272–12279
- Tyrode E, Johnson C M, Kumpulainen A, et al. Hydration state of non-ionic surfactant monolayers at the liquid/vapor interface: Structure determination by vibrational sum frequency spectroscopy. *J Am Chem Soc*, 2005, 127: 16848–16859
- Tyrode E, Johnson M C, Rutland W M, et al. Structure and hydration of poly(ethylene oxide) surfactants at the air/liquid interface. A vibrational sum frequency spectroscopy (VSFS) study. *J Phys Chem C*, 2007, 111: 11642–11652
- Warty M R, Tarbuck T L, Richmond G L. Vibrational sum-frequency studies of a series of phospholipid monolayers and the associated water structure at the vapor/water interface. *J Phys Chem B*, 2003, 107: 512–518
- Hirose C, Akamatsu N, Domen K. Formulas for the analysis of surface sum-frequency generation spectrum by CH stretching modes of methyl and methylene groups. *J Chem Phys*, 1992, 96: 997–1004
- Rao Y, Tao Y S, Wang H F. Quantitative analysis of orientational order in the molecular monolayer by surface second harmonic generation. *J Chem Phys*, 2003, 119: 5226–5236

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.