Ethylenediamine at Air/Liquid and Air/Silica Interfaces: Protonation Versus Hydrogen Bonding Investigated by Sum Frequency Generation Spectroscopy

MAN XU, DINGFANG LIU, AND HEATHER C. ALLEN[*]

Department of Chemistry, The Ohio State University, 100 West 18th Ave., Columbus, OH 43210

Phone (614) 292-4707; Fax (614) 292-1685; Email allen@chemistry.ohio-state.edu

SFG Spectra of EDA Aqueous Solutions (Polarization Combination sps)
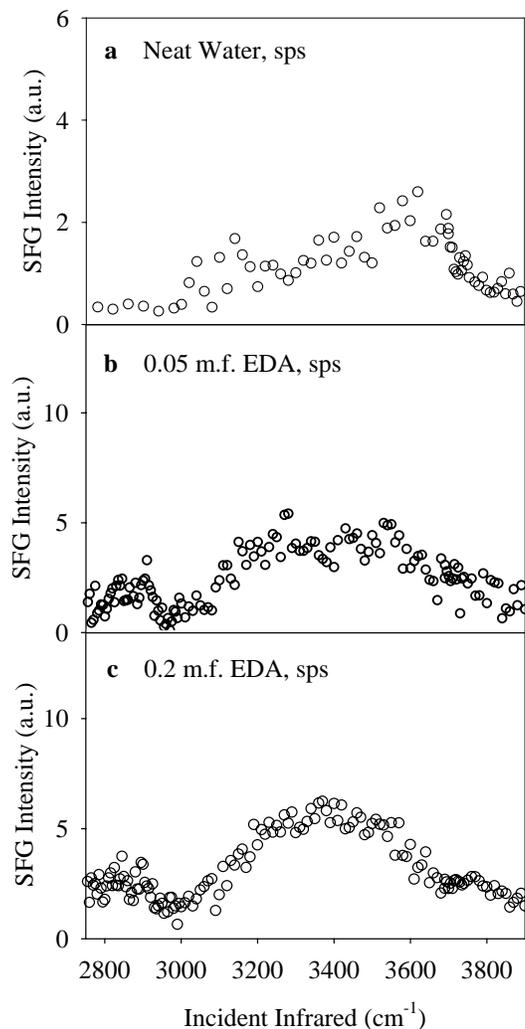
Figure S1. SFG spectra of a) neat water (scaled to the EDA experimental conditions); b) 0.05 m.f. ethylenediamine at the air/liquid interface; c) 0.2 m.f. ethylenediamine at the air/liquid interface with the sps polarization combination.

Curve-fitting of SFG Spectra

When several overlapping peaks contribute to the SFG spectral intensity, it is difficult to assign the accurate peak positions. Curve-fitting techniques can be used to determine the positions, amplitudes

and areas of the component peaks of a spectrum. In this paper, SFG spectra were analyzed with the peak-fitting function in Igor Pro 4.05A software using a home-written program to incorporate phase. The mathematical model describing the profile of bands is the Lorentzian model. Before performing curve-fits on the SFG spectra, curve-fitting of IR and Raman spectra of EDA and protonated EDA solutions were completed as references. During fitting processes of IR and Raman spectra, the second-derivative curves of the spectra were used to assist in determining the starting values of the peaks and their positions before each fitting operation. The minimum of the second-derivation indicates a change in the slope of the original data and, therefore, the position of the potential peaks. However, direct comparison of SFG spectra to IR and Raman spectra may be misleading. The IR or Raman intensity is the summation of each vibration's intensity, and, consequently, IR and Raman are non-coherent and there is no phase. In contrast, SFG is coherent. The SFG intensity (I_{SFG}) is proportional to the square of the summation of resonant ($\chi_v^{(2)}$) and non-resonant ($\chi_{NR}^{(2)}$) sum frequency terms as shown below in equations 2.1 and 2.2 (1).

$$I_{SFG} \propto \left| \chi^{(2)} \right|^2 = \left| \chi_{NR}^{(2)} + \sum_v \chi_v^{(2)} \right|^2 \tag{2.1}$$

$$\chi_v^{(2)} \propto \frac{A_v}{\omega_v - \omega_{IR} - i\Gamma_v} \tag{2.2}$$

where $\chi^{(2)}$ is the macroscopic second-order nonlinear susceptibility, which consists of resonant terms ($\chi_v^{(2)}$) and a non-resonant term ($\chi_{NR}^{(2)}$). A_v refers to the amplitude of the transition moment, ω_v is the frequency of the transition moment, and Γ_v describes the line-width of the transition. As a result, the relative phase of the SFG response and different non-resonant parameters are included in the curve-fitting of SFG spectra. Figure S2 and Table S1 show the curve-fitting results of SFG spectra in the CH stretching region.
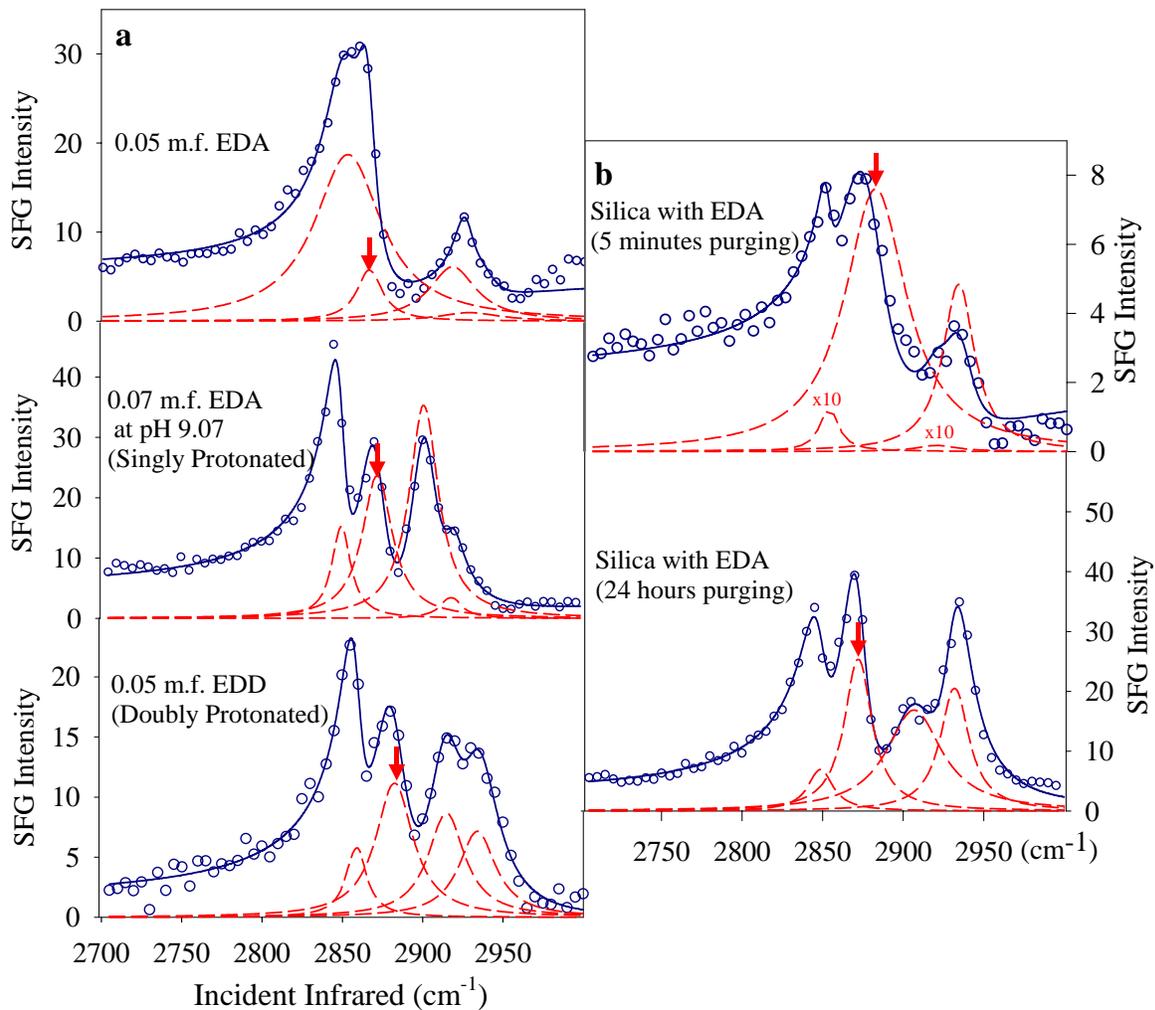
Figure S2. SFG spectra in the CH stretching region of a) 0.05 m.f. ethylenediamine at the air/liquid interface, 0.07 m.f. singly protonated ethylenediamine at the air/liquid interface, and 0.05 m.f. ethylenediamine dichloride at the air/liquid interface; b) ethylenediamine at the air/silica interface with 5 minutes purging (component peaks at 2852.0 cm^{-1} and 2918.9 cm^{-1} have been multiplied by 10), and ethylenediamine at the air/silica interface with 24 hours purging. Blue circles: experimental; blue solid lines: overall fits; red dashed lines: Lorentzian component peaks. The probe peak is denoted by the red arrow.

Table S1. Curve-fitting results of SFG spectra in the CH stretching region (all the component peaks are in phase).

	Non-resonant response		CH$_2$-SS				CH$_2$-AS			
	Real part	Imaginary part	Peak position (ω)	Amplitude (A)	Half width (Γ)	Area	Peak position (ω)	Amplitude (A)	Half width (Γ)	Area
0.05 m.f. EDA	-0.8	-0.9	2852.6	109.9	25.4	1334.6	2917.7	43.8	17.7	308.5
			2866.0	23.1	9.6	167.0	2928.3	22.4	22.9	59.9
0.2 m.f. EDA	-0.9	-0.95	2849.8	220.8	27.7	4892.7	2918.0	121.8	21.7	1900.1
			2861.2	40.4	9.2	536.9	2932.4	30.3	16.5	157.2
0.07 m.f. singly protonated EDA	-1.0	-1.0	2849.6	27.8	7.1	331.8	2900.9	65.7	11.0	1164.5
			2872.0	55.1	11.3	803.1	2917.6	14.9	7.9	84.1
0.05 m.f. EDD (doubly protonated EDA)	-0.8	-0.6	2858.8	18.8	7.8	138.0	2914.8	40.8	13.8	350.7
			2882.6	47.0	14.0	463.8	2934.0	37.4	14.0	287.9
Silica with EDA (5 min purging)	-0.9	-0.8	2852.0	2.5	7.1	2.7	2918.9	2.0	15.0	0.8
			2881.0	64.8	23.5	503.0	2932.8	26.2	12.0	170.4
Silica with EDA (24 hr purging)	-0.8	-1.0	2848.7	24.9	9.4	329.0	2906.8	85.9	20.9	835.8
			2872.1	52.1	10.3	961.0	2932.0	49.2	10.8	517.9

Speciation of EDA at Different pH

The species of EDA vary at different pH. The predominant species can be EDA, one NH$_2$ protonated (singly protonated) EDA or two NH$_2$ protonated (doubly protonated) EDA. To calculate the concentrations of each species at different pH values, the following equations are used (2):

$$[B] = \frac{B_T}{[H^+]^2 / K_{a1}K_{a2} + [H^+]/K_{a1} + 1} \tag{3.1}$$

$$[HB^+] = \frac{B_T}{[H^+]/K_{a2} + 1 + K_{a1}/[H^+]} \tag{3.2}$$

$$[H_2B^{2+}] = \frac{B_T}{1 + K_{a2}/[H^+] + K_{a1}K_{a2}/[H^+]^2} \tag{3.3}$$

where B refers to EDA, HB$^+$ is singly protonated EDA, and H$_2$B^{2+} refers to doubly protonated EDA. For EDA, $K_{a1}=10^{-10.71}$, $K_{a2}=10^{-7.56}$. The percentages of different EDA species at different pH values are

shown in Figure S3. By controlling the pH, the singly protonated EDA solution was obtained at pH 9.07, where singly protonated EDA accounts for 95% of all EDA species.
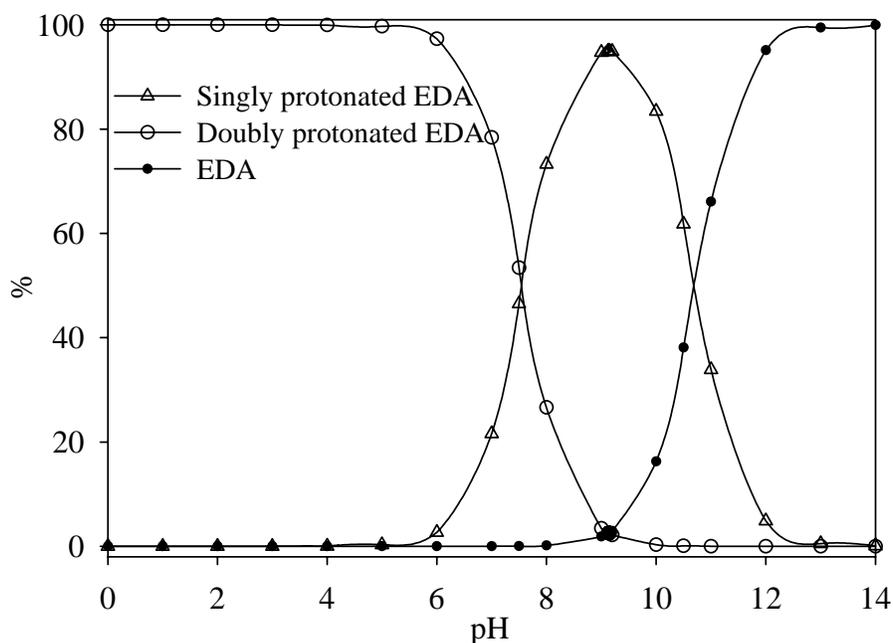
Figure S3. Percentages of EDA species at different pH values.

Orientation Calculations

The capability of determining molecular orientation is a significant advantage of SFG studies (3). Different components of $\chi^{(2)}$ are related to the spectroscopically active components of the molecular hyperpolarizability tensor $\beta^{(2)}$ by the average orientation angle of the functional group (3-7). The molecular symmetry determines the nonzero elements of $\beta^{(2)}$ (6). In the present work the methylene groups of ethylenediamine are treated as having a C_{2v} symmetry. For the methylene group, the nonzero SFG tensor elements of the symmetric stretch are β_{aac}, β_{bbc} and β_{ccc} that are related by $\beta_{aac} + \beta_{bbc} = 2\beta_{ccc}$ for methylene at the standard bond angle 109.5° (4, 6, 8). Though the bond angle in EDA is not exactly 109.5°, the value of $\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}$ remains a small number close to zero. For the antisymmetric mode, β_{aca} equals β_{caa} (4, 6, 8). The *abc* represents the molecule-fixed coordinate system.

The components of χ for the symmetric stretch (SS) are given by (6), χ is described in the surface-fixed (xyz) coordinate system:

$$\chi xxz\_SS(\theta) = \frac{1}{4} \cdot Ns \cdot (\beta_{aac} + \beta_{bbc} + 2\beta_{ccc}) \cdot \cos(\theta) + \frac{1}{4} \cdot Ns \cdot (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) \cdot \cos^3(\theta) \quad (4.1)$$

$$\chi xzx\_SS(\theta) = -\frac{1}{4} \cdot Ns \cdot (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) \cdot [\cos(\theta) - \cos^3(\theta)] \quad (4.2)$$

$$\chi zzz\_SS(\theta) = \frac{1}{2} \cdot Ns \cdot (\beta_{aac} + \beta_{bbc}) \cdot \cos(\theta) - \frac{1}{2} \cdot Ns \cdot (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) \cdot \cos^3(\theta) \quad (4.3)$$

For the antisymmetric stretch (AS), the components of χ are given by (5):

$$\chi xxz\_AS(\theta) = -\frac{1}{2} \cdot Ns \cdot \beta_{aca} \cdot [\cos(\theta) - \cos^3(\theta)] \quad (4.4)$$

$$\chi xzx\_AS(\theta) = \frac{1}{2} \cdot Ns \cdot \beta_{aca} \cdot \cos^3(\theta) \quad (4.5)$$

$$\chi zzz\_AS(\theta) = Ns \cdot \beta_{aca} \cdot [\cos(\theta) - \cos^3(\theta)] \quad (4.6)$$

where θ is the tilt angle from the surface normal.

$\chi xxz\_SS(\theta)$ and $\chi xxz\_AS(\theta)$ are related to the SFG spectra using the ssp polarization combination. According to previous work (4), the relations between β_{ccc}, β_{aac} and β_{caa} are $\beta_{aac} = 2 \cdot \beta_{ccc}$ and $\beta_{caa} = 1.053 \cdot \beta_{aac}$ for CH_2 with C_{2v} symmetry. Combined with the relationships $\beta_{aac} + \beta_{bbc} = 2\beta_{ccc}$ and $\beta_{aca} = \beta_{caa}$ shown above, and assuming that $\frac{1}{2} \cdot Ns \cdot \beta_{ccc} = 1.00\,ArbitraryUnit(a.u.)$, equation 4.1 and 4.4 can be greatly simplified:

$$\chi xxz\_SS(\theta) = 2 \cdot \cos(\theta) \quad (4.7)$$

$$\chi xxz\_AS(\theta) = -2.106 \cdot [\cos(\theta) - \cos^3(\theta)] \quad (4.8)$$

Here, absolute values of χ are used for the antisymmetric stretch.

$$\chi xxz\_AS(\theta) = \left| -2.106 \cdot [\cos(\theta) - \cos^3(\theta)] \right| \quad (4.9)$$

Figure S4 shows the dependence of second order susceptibilities on the tilt angle. The calculated tilt angle θ from the SFG intensity ratio of the symmetric and antisymmetric stretch are listed in Table S2.
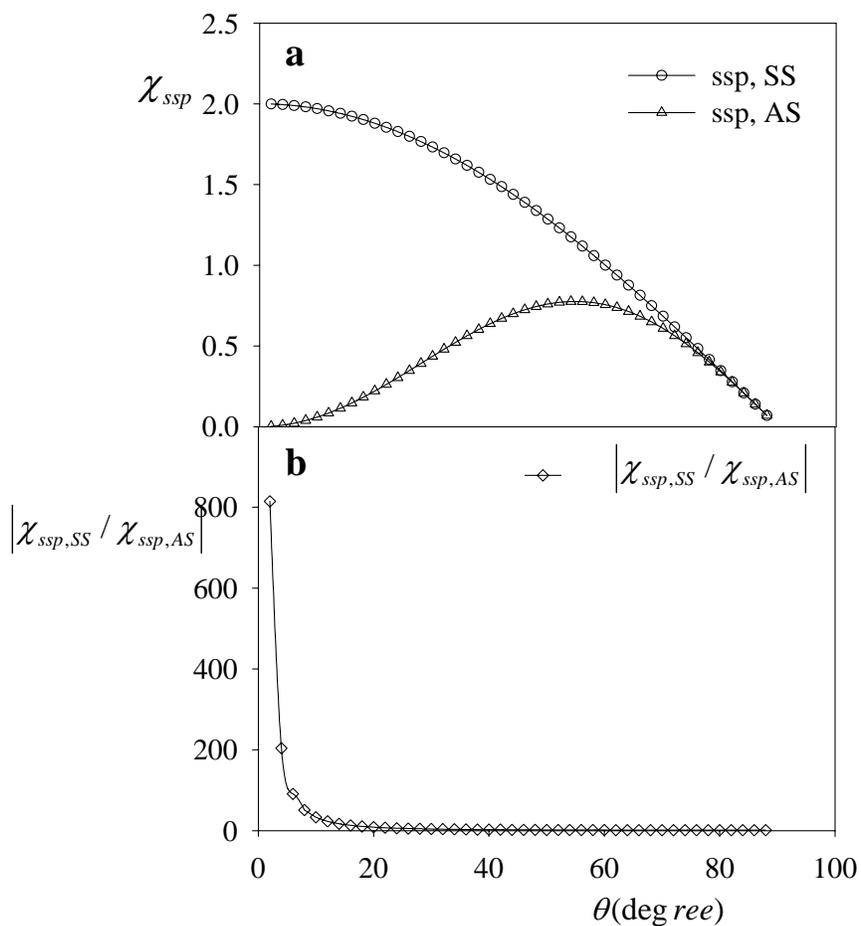
Figure S4. SFG intensities for the symmetric (SS) and antisymmetric (AS) stretch of methylene (a) and the ratio between them (b) as a function of tilt angle.

Table S2. Orientation calculation results of SFG spectra. (Error in θ was determined by the error in the reproducible fits.)

	A(SS)	A(AS)	A(SS)/A(AS)	χSS/χAS	Cos (θ)	θ (degree)
0.05 m.f. EDA	1502	368	4.08	2.02	0.7278	43±5
0.2 m.f. EDA	5430	2057	2.64	1.62	0.6445	50±3
Silica with EDA (5min)	506	171	2.96	1.72	0.6689	48±6
Singly protonated EDA	1135	1249	0.909	0.953	0.06211	86±4
EDD (doubly protonated EDA)	602	639	0.942	0.971	0.1473	82±2
Silica with EDA (24hr)	1290	1354	0.953	0.976	0.1647	81±7

A(SS): the area of CH_2-SS peaks; A(AS): the area of CH_2-AS peaks; χSS: the second order macroscopic nonlinear susceptibility of CH_2-SS; χAS: the second order macroscopic nonlinear susceptibility of CH_2-AS.

Surface Mole Fraction

The adsorption of a solute at the liquid/air interface, hence the surface mole fraction, is characterized by the relative adsorption ($\Gamma_{2,1}$) (9, 10). The relative adsorption is related to the surface tension (γ) through the Gibbs equation (9, 11):

$$\Gamma_{2,1} = -\frac{x(\frac{\partial \gamma}{\partial x})_{T,P}}{RT(1 + x\frac{\partial \ln f}{\partial x})} = \Gamma_2 - \Gamma_1 \frac{x}{1-x} \tag{5.1}$$

where x refers to the bulk mole fraction of ethylenediamine, f is the activity coefficient of EDA in the solution, R is the universal gas constant 8.314 J/(Kmol), T refers to the temperature, Γ_1 and Γ_2 refer to the surface excess concentrations of water and EDA, with the unit $\mu mol/m^2$. In the present paper, the surface tension values of ethylenediamine aqueous solutions were obtained by using a DeltaPi Tensiometer (Kibron Inc.) at ~297 K. According to the linear regression result of the experimental surface tension data (Figure S5a), $(\frac{\partial \gamma}{\partial x})_{T,P}$ is constant which equals –30.0. The activity coefficient f for

EDA in the binary system of EDA and water is predicted by using the UNIFAC group-contribution method (12, 13), as shown in Figure S5b. The relative adsorption $\Gamma_{2,1}$ versus bulk mole fraction of EDA is plotted in Figure S5c.

Assume the surface molecular areas of water (a_1) and EDA (a_2) are concentration independent, the following relationship exists based on the monolayer model.

$$N_{AV}(\Gamma_1 a_1 + \Gamma_2 a_2) = 10^{26} \tag{5.2}$$

where Γ_1 and Γ_2 are expressed in $\mu mol/m^2$, a_1 and a_2 are expressed in $Å^2$, and N_{AV} is Avogadro's number. a_1 is 8 $Å^2$ for water according to literature (10). a_2 is estimated to be 14 $Å^2$ for EDA using the relative molecular surface area values provided by Gmehllng et al. (13), which agrees with the experimental value (14). The surface mole fraction (m.f.$_s$) can be obtained by:

$$m.f._s = \frac{\Gamma_2}{\Gamma_2 + \Gamma_1} \tag{5.3}$$

Figure S5d shows the surface mole fraction of EDA versus the bulk mole fraction of EDA.
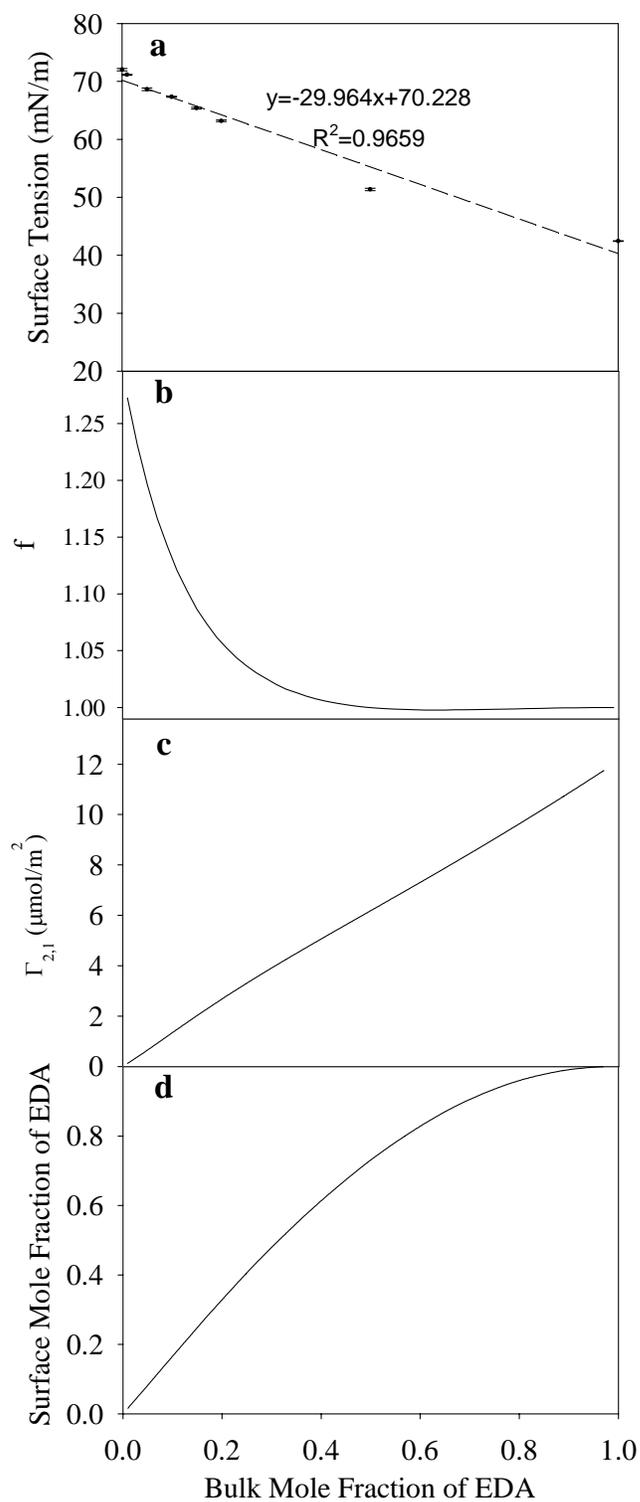
Figure S5. (a) Surface tension values versus bulk mole fraction of ethylenediamine. Data points: experimental data with error bars; dashed line: linear regression. (b) Activity coefficient (f) of ethylenediamine in aqueous solutions. (c) Relative adsorption ($\Gamma_{2,1}$) of ethylenediamine in aqueous solutions. (d) Surface mole fraction of EDA versus bulk mole fraction of EDA.

SFG Spectra of Reference Systems (Polarization Combination ssp)
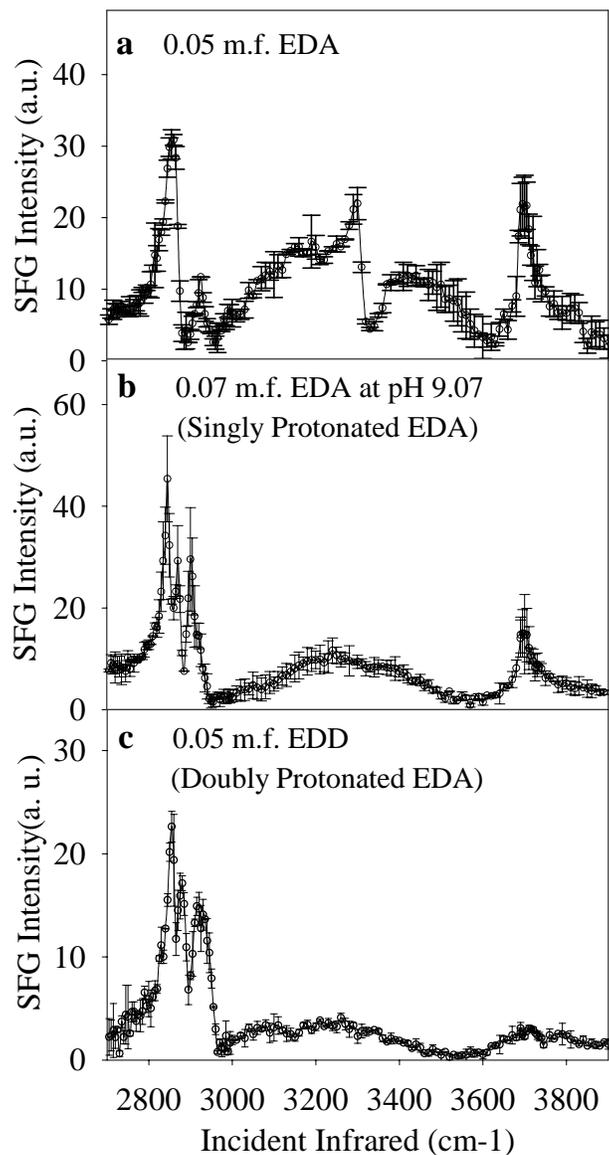
Figure S6. SFG spectra of three reference systems: a) 0.05 m.f. ethylenediamine at the air/liquid interface; b) 0.07 m.f. singly protonated ethylenediamine at the air/liquid interface; c) 0.05 m.f. ethylenediamine dichloride at the air/liquid interface.

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