Supporting Information for

Anomalous Effective Polarity of an Air/Liquid Mixture Interface: A Heterodyne-Detected Electronic and Vibrational Sum Frequency Generation Study

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S1. Sample Preparation

N,*N*-diethyl-*p*-nitroaniline (DEPNA) was purchased from Frinton Laboratories and used as received. *N*,*N*-dimethylformamide (DMF; HPLC grade) and cyclohexane (HPLC grade) were purchased from Wako and used as received. 1,4-dioxane (99.8%, anhydrous) was purchased from Aldrich and used as received. Purified water (Millipore, 18.2 MΩ cm resistivity) was used. The concentration of DEPNA for HD-ESFG measurements was 7×10^{-5} mol dm^{-3}. The UV-visible absorption spectra of the samples were measured by using a commercial spectrometer (U3310, Hitachi).

Figure S1 shows relationship between the E_N^T polarity scale[1] and the peak wavelength of the UV-visible absorption spectra of DEPNA in water ($E_N^T = 1.000$), DMF ($E_N^T = 0.386$), 1,4-dioxane ($E_N^T = 0.164$), and cyclohexane ($E_N^T = 0.006$). By using this relationship, the E_N^T polarity scales of the bulk mixtures and the air/mixture interfaces were determined.

S2. Surface Tension

To determine the surface excess of DMF at the interface, the surface tension of the binary mixture of water and DMF was measured by using a surface tension meter (KSV Instruments, Sigma 701) with a Wilhelmy plate. The surface excess was calculated on the basis of the Gibbs adsorption isotherm. Figure S2 shows the surface excess of DMF at the air/mixture interface as a function of a DMF mole fraction in the bulk.

The local DMF fraction at the interface was calculated by converting the surface excess (molecules per area) into the local concentration (mole per volume) of DMF on the assumption that the thickness of the interface is 1 nm. This assumption is compatible with the density profile of water along the interface normal calculated by molecular dynamics simulation.[2,3] The local concentration of water at the interface was assumed to be the half of the bulk concentration, because the density of water drops from the bulk concentration to zero at the Gibbs dividing surface. Thus, the local DMF fraction is given by the local concentration of DMF divided by the sum of the local concentrations of water and DMF.

S3. HD-ESFG

The experimental details of heterodyne-detected electronic sum frequency generation (HD-ESFG) spectroscopy were described previously.[4] In brief, the light source of the apparatus was a 3.5-mJ Ti:sapphire regenerative amplifier system (Spectra Physics, Spitfire Pro XP, 120 fs, 1 kHz). A portion of the amplifier output was used as a narrow-band ω_1 (795 nm) pulse, and the other was focused into water to generate a broad-band ω_2 (540 nm ~ 1.2 µm) pulse. The ω_1 and ω_2 pulses were noncollinearly focused onto the same spot at the sample surface. When the ω_1 and ω_2 pulses were temporally overlapped, the sum frequency ($\omega_1 + \omega_2$) was generated at the surface. The ω_1, ω_2, and $\omega_1 + \omega_2$ pulses were again focused by a spherical concave mirror onto a GaAs(110) surface to generate the sum frequency of ω_1 and ω_2 once more. A fused-silica glass plate of 1-mm thickness was placed on the optical path between the sample and the concave mirror. The glass substrate delayed the $\omega_1 + \omega_2$ pulse relative to the reflected ω_1 pulse by 170 fs due to frequency-dependent differences in the group velocity. This delay resulted in the time difference between the $\omega_1 + \omega_2$ pulse generated from the sample and that from GaAs. The $\omega_1 + \omega_2$ pulse from the sample and that from GaAs propagated collinearly and sequentially through an analyzer, and entered into a polychromator. After spectrally dispersed, the $\omega_1 + \omega_2$ sum frequency light was detected by a multichannel detector (Roper Scientific, Spec-10:2KBUV). Interference fringes between the two $\omega_1 + \omega_2$ pulses were superimposed on the detected spectra. The Fourier analyses of the interference fringes yielded the complex $\chi^{(2)}$ spectrum of the sample surface. The $\omega_1 + \omega_2$, ω_1, and ω_2 pulses were s-, p-, and s-polarized, respectively, which is conventionally abbreviated to the SPS polarization combination.

S4. HD-VSFG

The experimental details of heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy were described previously.[5,6] In brief, the light source of the apparatus was a 5.0-mJ Ti:sapphire regenerative amplifier system (Spectra Physics, Spitfire

Ace, 80 fs, 1 kHz). A portion of the amplifier output was used as a narrow-band ω_1 (center: 795 nm, width: 24 cm^{-1}) pulse after passing through an interference filter, and the other pumped an optical parametric amplifier (Spectra Physics, TOPAS Prime) to generate a broadband IR ω_2 (center: 2750, 3000, and 3400 nm, width: 300 cm^{-1}) pulse. The ω_1 and ω_2 pulses were noncollinearly focused on and transmitted through an ultrathin y-cut quartz (Crystal Base Co., Ltd.) having 10 μm thickness. When the ω_1 and ω_2 pulses were temporally overlapped, the sum frequency ($\omega_1 + \omega_2$) was generated. The ω_1, ω_2, and $\omega_1 + \omega_2$ pulses were again focused by a spherical concave mirror onto the sample surface to generate the sum frequency of ω_1 and ω_2 once more. A fused-silica glass plate of 2-mm thickness was placed on the optical path of the $\omega_1 + \omega_2$ pulse between the concave mirror and the sample. The glass substrate delayed the $\omega_1 + \omega_2$ pulse relative to the transmitted ω_1 and ω_2 pulses by 3.4 ps. This delay resulted in the time difference between the $\omega_1 + \omega_2$ pulse generated from the y-cut quartz and the sample. The $\omega_1 + \omega_2$ pulse from the *y*-cut quartz and that from the sample propagated collinearly and sequentially through an analyzer, and entered into a polychromator. After spectrally dispersed, the $\omega_1 + \omega_2$ sum frequency light was detected by a multichannel detector (Princeton Instruments, Spec-10:2KB). Interference fringes between the two $\omega_1 + \omega_2$ pulses were superimposed on the detected spectra. The Fourier analyses of the interference fringes yielded the complex $\chi^{(2)}$ spectrum of the sample surface. Three complex $\chi^{(2)}$ spectra were measured with different ω_2 and they were combined to fully cover the CH and OH stretch regions. The $\omega_1 + \omega_2$, ω_1, and ω_2 pulses were s-, s-, and p-polarized, respectively, which is conventionally abbreviated to the SSP polarization combination.

References

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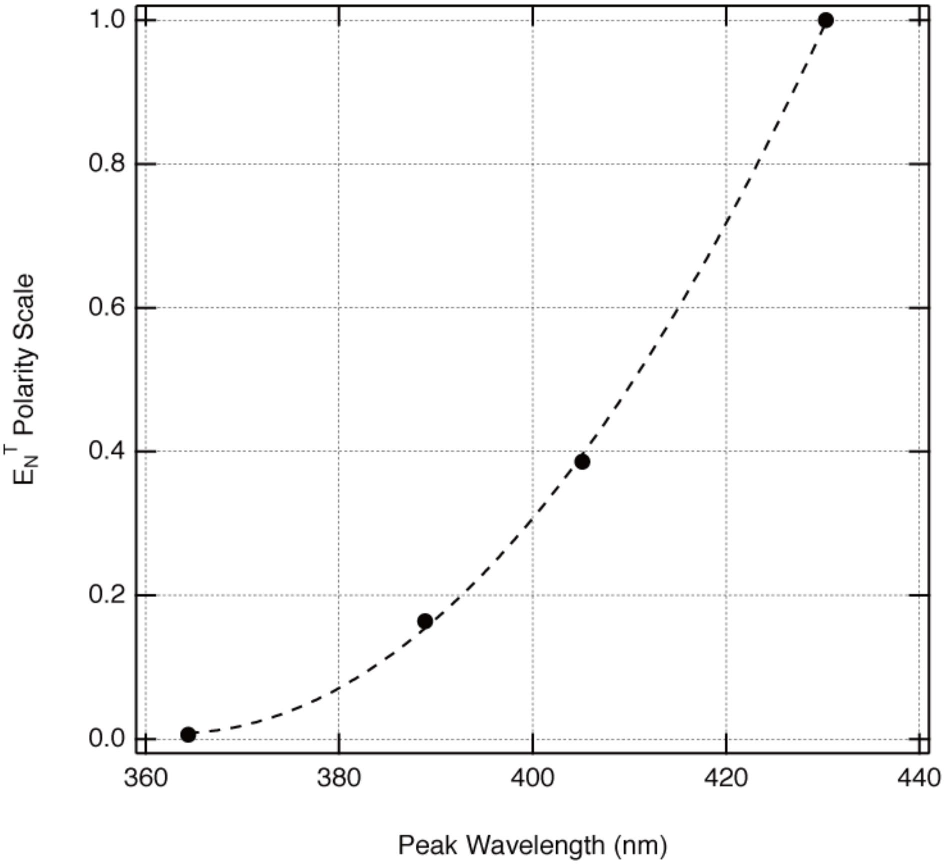

Figure S1. Relationship between the $E_N{}^T$ polarity scale and the peak wavelength of the UV-visible absorption spectra of DEPNA in water ($E_N{}^T$ = 1.000), DMF ($E_N{}^T$ = 0.386), 1,4-dioxane ($E_N{}^T$ = 0.164), and cyclohexane ($E_N{}^T$ = 0.006). Solid circles represent experimental data, and the dashed line stands for a fit. A polynomial up to a square term was used for fitting.

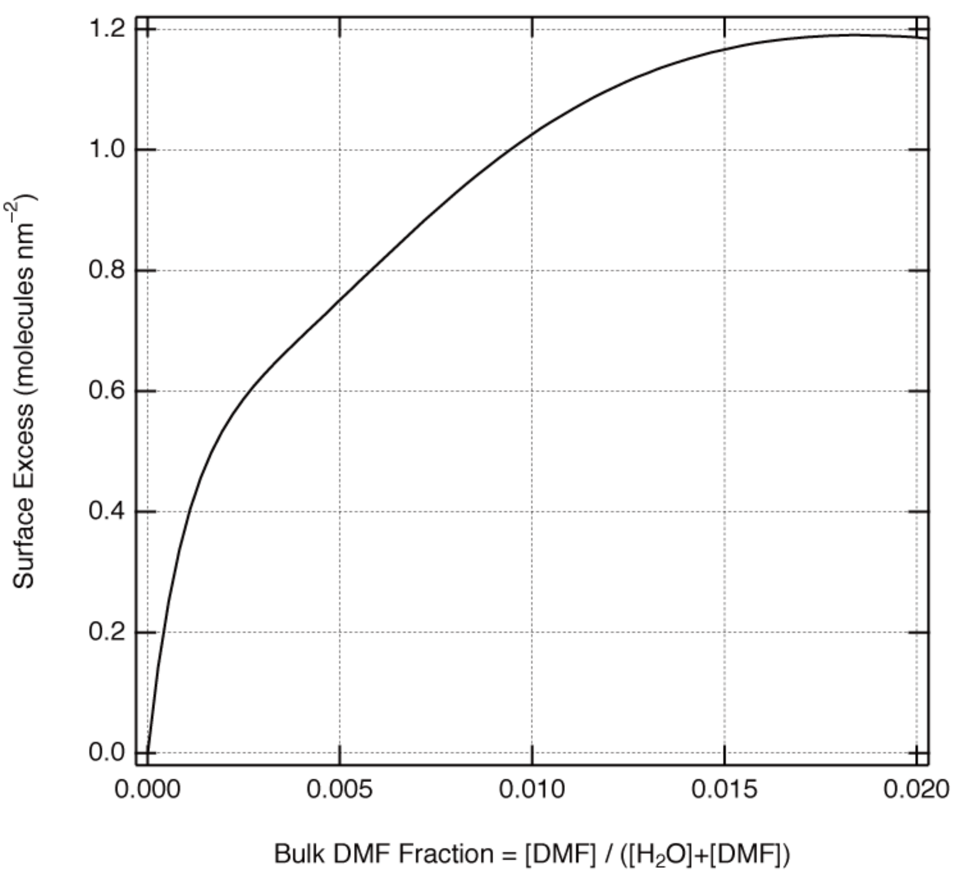

Figure S2. Surface excess of DMF at the air/mixture interface as a function of a DMF mole fraction in the bulk.