

1P059

Polarity and Solvent Environment at Air/Solvent Mixture Interfaces Studied by Electronic Spectral Shift of a Solvatochromic Dye

(Molecular Spectroscopy Laboratory, RIKEN)

○Sudip Kumar Mondal, Shoichi Yamaguchi, and Tahei Tahara

Recently, our group developed heterodyne detected electronic sum frequency generation (HD-ESFG) for measuring electronic spectra of molecules adsorbed at interfaces.^{1a} This technique gives very high quality electronic $\chi^{(2)}$ spectra with real and imaginary part separately. In our previous studies it was found that the air/water interface is less polar than bulk water, but more inhomogeneous as a solvation environment than bulk solvents of its equal polarity.^{1b-c} Now we are interested in the solvation environment at the air/liquid interface of solvent mixtures containing water and a less polar solvent. It is well known that, the polarity of such a solvent mixture is less than that of water and as a result the electronic spectra of coumarin 110 (C110) show a blue shift. So, it is expected that the imaginary $\chi^{(2)}$ ($\text{Im}[\chi^{(2)}]$) spectra of C110 at the air/solvent mixture interfaces will be further blue shifted from the spectrum at the air/water interface.

In the present work, we applied HD-ESFG spectroscopy to C110 at the air/solvent mixture interfaces. We chose DMF, DMSO, dioxane, and propanol as less polar solvent of the mixtures, and studied the shift of $\text{Im}[\chi^{(2)}]$ spectra of C110. Figure 1 shows the $\text{Im}[\chi^{(2)}]$ spectra of C110 at the air/solvent mixture interfaces with the variation of less polar solvent concentrations in the mixtures. For all the solvent mixtures, unexpectedly, a clear red shift from the spectrum at the air/water interface is observed. It indicates that at air/solvent mixture interfaces C110 experiences more polar environment than the air/water interface. The UV-visible spectra of corresponding bulk studies are shown in Figure 2. It is found that for all solvent mixture, there is also a red shift before blue shift is observed, but the amount of the red shift is much less than in the corresponding interface spectra.

At the air/water interface a C110 molecule gets stabilized by putting its hydrophilic part into water and sticking the hydrophobic part out in the air. From surface tension studies of solvent mixtures, it is found that less polar solvents are surface active and after certain concentration the less polar solvent covers the entire water surface. The solubility of C110 in less polar solvents is much higher than in

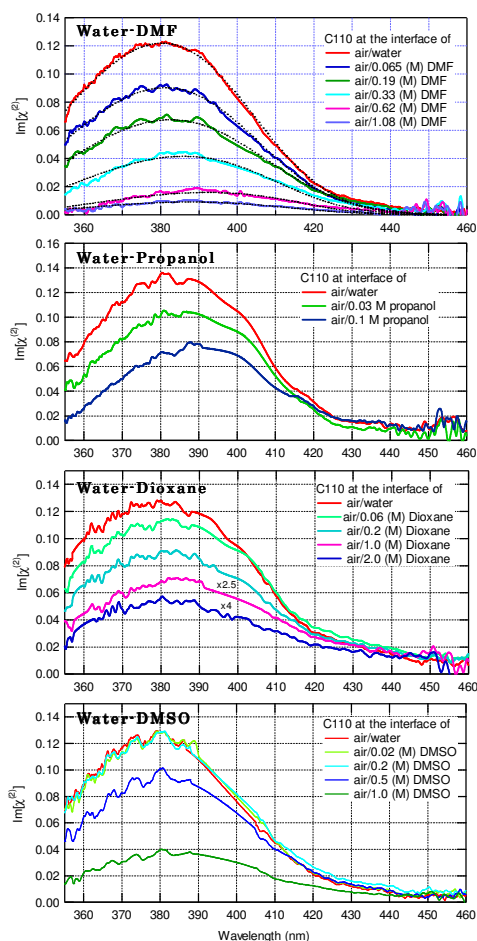


Figure 1: Imaginary $\chi^{(2)}$ spectra of C110 at air/liquid interfaces of solvent mixtures containing water and DMF, Propanol, Dioxane, DMSO.

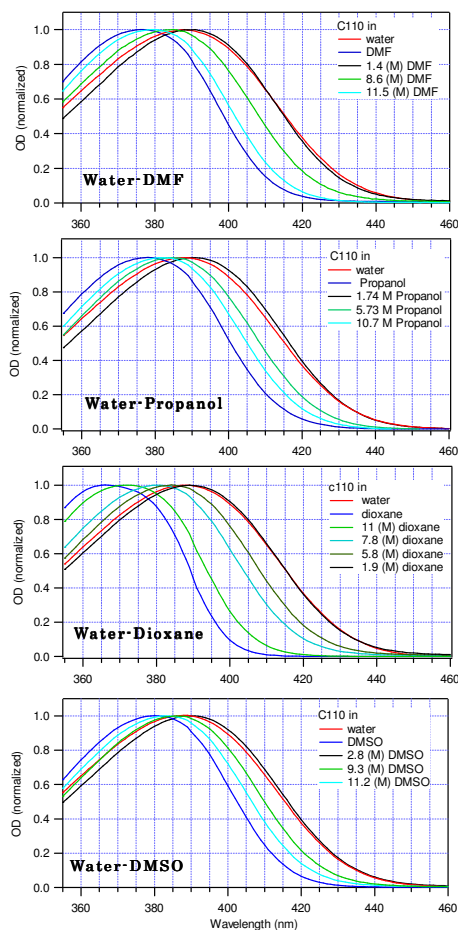


Figure 2: UV-visible absorption spectra of C110 in bulk solvent mixtures containing water and DMF, Propanol, Dioxane, DMSO.

water. So, we can conclude that the C110 molecule at the interface gets stabilized more and more when less polar solvents cover it gradually. C110 will increasingly feel bulk-like environment in which the spectra are red shifted compared to that in air/water interface. The drastic decrease of signal intensity of $\text{Im}[\chi^{(2)}]$ spectra (Figure 1) at the air/solvent mixture interfaces is also a indication of bulk-like environment around C110. Thus, we conclude that C110 at the air/solvent mixture interfaces experiences a solvation environment which is very similar to that in the corresponding bulk solvent mixtures.

References

1. (a) Yamaguchi, S.; Tahara, T. *J. Chem. Phys.* **2008**, *129*, 101102. (b) Sen, S.; Yamaguchi, S.; Tahara, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 6439. (c) Mondal, S. K; Yamaguchi, S.; Tahara, T. *in preparation*.