Second harmonic generation measurements of molecular orientation and coadsorption at the interface between two immiscible electrolyte solutions

Daniel A. Higgins, Roberta R. Naujok and Robert M. Corn

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396, USA

Resonant optical second harmonic generation (SHG) is obtained from monolayers of 4-*n*-octyloxybenzoic acid (OBA) and *n*-octyl-4-hydroxybenzoate (OHB) adsorbed at the water/1,2-dichloroethane interface. The polarization dependence of the SHG from pure monolayers of OBA and OHB indicates that the molecular axis of the OBA molecules is tilted 6° closer to the surface normal than that of the OHB molecules. The SHG from a series of mixed monolayers of OBA and OHB exhibits interference effects that demonstrate that the dipole moments of the coadsorbed molecules are oriented in opposite directions at the interface.

1. Introduction

The study of liquid–liquid interfaces is motivated by their numerous applications in separation science, solar energy conversion, and the modeling of biological and other complex chemical systems. A complete interpretation of the chemistry that occurs in such systems requires extensive knowledge of interfacial processes such as solvent mixing, solute transport, and chemical reactions occurring at these surfaces. All of these processes are controlled by the interfacial molecular architecture; therefore an understanding of the adsorption, orientation, and organization of both solute and solvent molecules within the interfacial region is the first step in the control and design of these systems. One type of liquid–liquid interface which has been of interest since the turn of the century is the interface between two immiscible electrolyte solutions (ITIES) [1]. In the past twenty years a great deal of information on the interfacial structure of the ITIES has been obtained from a number of elegant surface tension and electrochemical measurements [1–4]. However, to date there have been a limited number of spectroscopic studies of monolayer films at liquid–liquid interfaces [5–13].

A major problem in the spectroscopic study of liq-uid–liquid interfaces is the separation of the optical response of the interface from that of the adjacent bulk media. Optical second harmonic generation (SHG) is an inherently surface-sensitive process that overcomes this difficulty because it is electric-dipole forbidden in bulk centrosymmetric media [14]. For the interface between two centrosymmetric media, such as the interface between two liquids, only the molecules which participate in the asymmetry of the interface contribute to the SHG. When the nonlinear response of the interface is dominated by resonant molecular contributions, SHG measurements can be used to determine the relative surface coverage and average molecular orientation within an adsorbed monolayer. A comprehensive study of surfactant adsorption at the ITIES utilizing SHG was recently presented [13]. However, to date no SHG studies of molecular orientation at the ITIES have been published, although the methodology for such studies, and its application at other interfaces, is well documented [15–17].

In this Letter, we report the application of surface SHG measurements to the study of molecular orientation and coadsorption of monolayer films at the ITIES. The polarization dependence of the resonant SHG from a monolayer of molecules adsorbed at the water/1,2-dichloroethane (DCE) interface is used

in conjunction with a previously developed methodology [18,19] to determine the average molecular orientation within the monolayer. Specifically, the average molecular orientation is determined for two different monolayers, one comprised of pure 4-n-octyloxybenzoic acid (OBA) and the other comprised of pure n-octyl-4-hydroxybenzoate (OHB). Further information on the relative alignment of the dipole moments of these two molecules, as well as their relative adsorption strengths, is obtained by measuring the SHG from a series of mixed monolayers of OBA and OHB. Being nearly identical in molecular and electronic structure, with the important exception of the direction of their dipole moments, these molecules are ideal candidates for observing differences in the structures of their monolayer films.

2. Experimental considerations

The 4-n-octyloxybenzoic acid (Aldrich) and n-octyl-4-hydroxybenzoate (Lancaster Synthesis) used in these experiments were purified by passage through silica gel in ethyl acetate/hexane solution. The structures of OBA and OHB are shown in fig. 1. The supporting electrolytes (Fluka) used in these experiments were NaCl, Na$_2$HPO$_4$, and tetrabutylammonium tetraphenylborate (TBATPB) and were used as received. Millipore-filtered water was used to prepare the aqueous phase (50 mM NaCl, 25 mM Na$_2$HPO$_4$, adjusted to pH 2.2), and SpectraAR grade (Mallinckrodt) DCE was used as the organic phase (1 mM TBATPB).

The sample apparatus was the same as that used in previous experiments [12,13]. Exactly 25 mL of organic solution and 20 mL of aqueous solution were used in each experiment. The two phases were pre-equilibrated prior to use by vigorously mixing in a separatory funnel. The solutions were then allowed to equilibrate in the spectrochemical cell for $\approx$ 30 min prior to the start of an experiment. Neither OBA nor OHB partitioned into the aqueous phase to a significant extent, as determined by UV–VIS spectroscopy.

The laser system and optical apparatus used in these experiments is similar to that described previously [13,18,19]. Measurements of the SHG from the water/DCE interface were made with the 532 nm output of a Nd:YAG laser ($\approx$ 3 mJ per pulse, 10 Hz rep rate, 10 ns pulse width). The fundamental light was polarized by passage through a polarizer (Special Optics 10^{-5} extinction ratio) and a 532 $\lambda/2$-plate (Special Optics), focused just above the air/water interface, and passed through a UV-blocking filter (Schott Glass GG-475) prior to incidence (70° from the surface normal at the air/water interface) on the interface. The SHG was separated from the residual fundamental light reflected from the water/DCE interface with a UV-passing filter (Schott Glass UG-5). The polarization of the SHG was selected with a UV-polarizer (Karl Lambrecht 10^{-5} extinction ratio). UV mirrors and a 0.175 m monochromator were used to collect the SHG and were calibrated to correct for any polarization-dependent effects. Detection was accomplished with a PMT and boxcar averager [18,19].

3. Results and discussion

Although OBA and OHB are structurally very similar, the two molecules possess certain key differences that cause them to form distinct monolayer structures at the water/DCE interface. Both are highly surface-active and form monolayers of
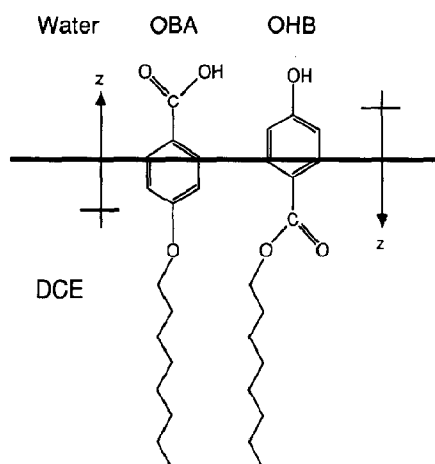

Fig. 1. Molecular structures of OBA and OHB at the water/DCE interface. The groundstate molecular dipole moments for each molecule are also shown with the positive molecular z axis defined in relation to the dipole moment as shown.

$\approx 5 \times 10^{13}$ molecule cm^{-2} at 20 mM bulk concentration, as determined by interfacial tension measurements [13]. The surface-activities are similar for the two molecules as both include hydrophobic (C_8 alkyl chain) and hydrophilic (acid group in OBA, hydroxy group in OHB) elements (see fig. 1). Slight differences in the hydrophilic groups on the benzene rings of OBA and OHB may contribute to differences in the orientation of the molecules within the monolayer through different hydrogen bonding interactions. On the other end of the p-hydroxybenzoic acid head-group, the greater hydrophilicity of the ester linkage of OHB over the ether linkage of OBA may also cause differences in the structures of the two monolayers. Further differences in the molecular orientation may result from different packing structures within the monolayers. In addition, the connection of the alkyl chain to opposite ends of the head-group in OBA and OHB suggests that their head-groups, and thus their ground-state dipole moments, will align in opposite directions when adsorbed to the water/DCE interface. If the dipole moments are so aligned, each molecule's orientation will be further affected by the interaction of the dipoles with the static electric fields present at the ITIES.

In addition to the similarities in the molecular structures of OBA and OHB, their electronic properties are also very similar, as demonstrated by their respective UV–VIS spectra shown in fig. 2. These re-
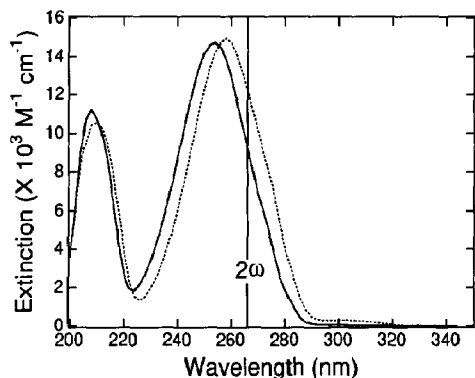
sults suggest that the dielectric constants of OBA and OHB monolayers, which are required for the molecular orientation calculation, are approximately equal; the validity of this assumption was verified by a Kramers–Kronig calculation utilizing these spectra [18,19]. Similar results were found for the nonlinear electronic properties of these molecules. π electron calculations of the molecular nonlinear polarizability tensor, β, were performed for each molecule [19]; the results show only slight differences in their second-order nonlinear responses [20]. From these theoretical calculations, both molecules are found to have large resonantly enhanced nonlinear polarizabilities at 266 nm which are dominated by contributions from the β_{zzz} and β_{zxx} tensor elements. These electronic similarities greatly facilitate the measurement of orientational differences in the two monolayers.

As expected from the previous discussion, a large resonant SHG signal at 266 nm was observed from the monolayers of OBA and OHB adsorbed at the water/DCE interface. This SHG signal was larger than the SHG from the interface in the absence of any specifically adsorbed species by more than an order of magnitude. In cases where the SHG from the interface is dominated by such resonant molecular contributions, the polarization dependence of the SHG can be used to measure the average molecular orientation of an adsorbed species. The average orientation calculation is performed by first obtaining the values of the non7zero elements of the macroscopic surface nonlinear susceptibility tensor $\chi^{(2)}$, as described by [21]

$$I_s(2\omega) \propto |a_1 \chi_{XXZ} \sin 2\gamma|^2 I(\omega)^2, \tag{1}$$

$$I_p(2\omega) \propto |(a_2 \chi_{XXZ} + a_3 \chi_{ZXX} + a_4 \chi_{ZZZ}) \cos^2\gamma$$
$$+ a_5 \chi_{ZXX} \sin^2\gamma|^2 I(\omega)^2, \tag{2}$$

where γ is the polarization angle of the incident fundamental light measured relative to the plane of incidence, $I_p(2\omega)$ and $I_s(2\omega)$ are the SHG intensities polarized in the p (parallel to the plane of incidence) and in the s (perpendicular to the plane of incidence) directions, and the a_i terms are constants based on the Fresnel coefficients of the interface and include the dielectric constants of the monolayer [19,22–24]. The polarization dependence of the SHG from separate monolayers of OBA and OHB

Fig. 2. UV–VIS spectra for OBA (——) and OHB (– – –) in dilute ethanolic solution. The vertical line in the plot shows the position of the second harmonic at 266 nm, indicating that the SHG from monolayers of these two molecules will be resonantly enhanced. The similarity of the spectra for the two molecules suggests that their electronic structures are nearly identical.

adsorbed to the water/DCE interface is plotted in fig. 3. From these SHG polarization results, the values of χ_{xxz}, χ_{zxx}, and χ_{zzz} can be determined, if the dielectric constants of the monolayer at the fundamental and second harmonic wavelengths are known. In these experiments, a Kramers–Kronig analysis of the UV–VIS absorption spectra was used to estimate the monolayer dielectric constants [18,19], the magnitudes of which were estimated to be 2.0 at the fundamental and 3.1 at the second harmonic.

Once the values of the nonzero elements of $\chi^{(2)}$ have been determined, both the molecular orientation parameter $D = \langle \cos^3\theta \rangle / \langle \cos\theta \rangle$ (where θ is the orientation angle between the molecular axis and the surface normal, as shown in fig. 3) and the relative contributions of β_{zzz} and β_{zxx} can be calculated from the appropriate equations relating the elements of
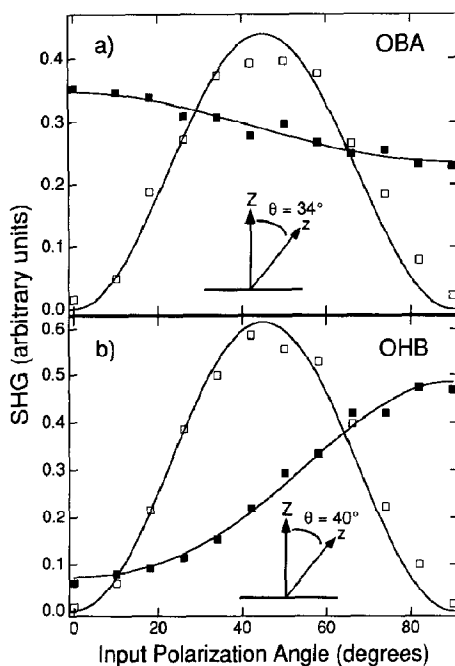

Fig. 3. Polarization dependence of the SHG from OBA and OHB monolayers at the ITIES. The s-polarized ($\square$) and p-polarized ($\blacksquare$) SHG is shown. The solid lines are fits to the data used to calculate values for the elements of $\chi^{(2)}$, which are in turn used to calculate the average molecular orientation within the monolayer. The average orientation angles θ for each molecule, utilizing the assumptions given in the text, are also shown and indicate that the molecular axis of OBA is aligned closer to the surface normal than that of OHB.

$\chi^{(2)}$ to those of β [18,19,25]. From the SHG results presented in fig. 3, it was calculated that $D = 0.69 \pm 0.03$ for OBA while $D = 0.59 \pm 0.03$ for OHB. Assuming that all molecules are adsorbed on the surface at the same angle, these results correspond to orientation angles θ of $34° \pm 2°$ and $40° \pm 2°$ for OBA and OHB, respectively, assuming a random distribution in the angle of rotation about the molecular axis [19]. The observed orientation difference of $6°$ for the two molecules is a direct result of the dramatically different p-polarized SHG curves for OBA and OHB, as shown in fig. 3. Information on the relative contributions of the dominant β tensor elements can also be obtained from the SHG polarization dependence; in these experiments, the SHG from both molecules was determined to be dominated by the β_{zzz} component of the molecular nonlinear polarizability, with approximately a 10% contribution from β_{zxx}. If β_{zzz} is assumed to be the only nonzero molecular nonlinear polarizability element the calculated dielectric constants must be independently adjusted to allow for a proper fit of the data. In this case $D = 0.63$ for OBA and $D = 0.56$ for OHB. Finally, it should be noted that the orientation calculation employs the approximate values for the dielectric constants calculated above. A variation in the dielectric constants of $\pm 20\%$ yields a $3°$ change in the absolute orientation angles of OBA and OHB, while the difference between their orientation angles changes by only $0.2°$. These results conclusively show that the molecular axis of OBA is oriented closer to the surface normal than that of OHB. The observed difference in the orientations for these two molecules is consistent with the structural differences discussed earlier.

While the SHG from pure monolayers of OBA and OHB was used above to measure the average angle between the molecular axis and surface normal, the magnitude of the SHG from mixed monolayers of OBA and OHB adsorbed at the water/DCE interface was used to verify that the dipole moments of the two molecules are aligned in opposite directions (see fig. 1). Similar measurements, based on the determination of the phase of the SHG from a monolayer, have been accomplished previously by either the interference of the SHG from a monolayer with that from a quartz crystal [19,26], or by the interference of the SHG from two monolayers deposited on op-

posite sides of a transparent substrate [27,28]. In the experiments presented here, the interference of the SHG from OBA with that from OHB adsorbed simultaneously in a series of mixed monolayers at the water/DCE interface was used to make this determination. If the dipole moments of OBA and OHB are aligned in opposite directions as expected, then the SHG from the two molecules should interfere destructively and should pass through a minimum at equal surface concentrations of OBA and OHB (assuming the molecular orientations and electronic structures are identical). Alternatively, if the dipole moments are aligned in the same direction, the SHG from the interface should be independent of the relative surface concentrations of OBA and OHB (assuming constant total surface coverage). The SHG results for a series of mixed monolayers of varying bulk concentrations of the molecules are plotted in fig. 4. Destructive interference is observed, indicating that the SHG from OBA is $\approx 180°$ out of phase with that from OHB. These results conclusively demonstrate that the dipole moments of the two molecules are aligned in opposite directions at the water/DCE interface.

A simple model for this interference effect, assuming equal nonlinear polarizabilities and orientations for both molecules, is given by:

$$I_{SHG} \propto (\Gamma_{OBA} - \Gamma_{OHB})^2, \tag{3}$$

where Γ_{OBA} and Γ_{OHB} are the surface concentrations of the two molecules. These surface concentrations can be estimated from a competitive Langmuir adsorption isotherm [29], assuming equal adsorption strengths and maximum surface coverages for the two molecules. The theoretical curve obtained from eq. (3) is plotted as a solid line in fig. 4 and demonstrates that this model is qualitatively correct. In addition, the observation that the minimum in the experimental SHG curve occurs at nearly equal bulk concentrations of OBA and OHB validates the assumption that the two molecules have approximately equal adsorption strengths.

4. Conclusions

In summary, we have demonstrated that the SHG from monolayers adsorbed at the ITIES can be used to determine the average molecular orientation of pure and mixed monolayers of nonlinearly active compounds. Specifically, the polarization-dependence of the resonant SHG from pure monolayers of OBA and OHB adsorbed at the water/DCE interface was used to determine the average molecular orientation of the molecules within the monolayer. From these orientation results, it was shown that the molecular axis of OBA is oriented 6° closer to the surface normal than that of OHB. The dramatic difference observed in the p-polarized SHG curves for the two molecules highlights the sensitivity of the polarization-dependent results to differences in the average orientations of molecules adsorbed at the ITIES. Furthermore, it was demonstrated that the SHG from OBA destructively interferes with the SHG from OHB in a series of mixed monolayers. This interference effect proves that the ground-state dipole moments of OBA and OHB are aligned in opposite directions in monolayer films at the water/DCE interface. Finally, a simple model based on a competitive Langmuir adsorption isotherm was shown to qualitatively describe the SHG from the mixed monolayers. Experiments are currently being per-
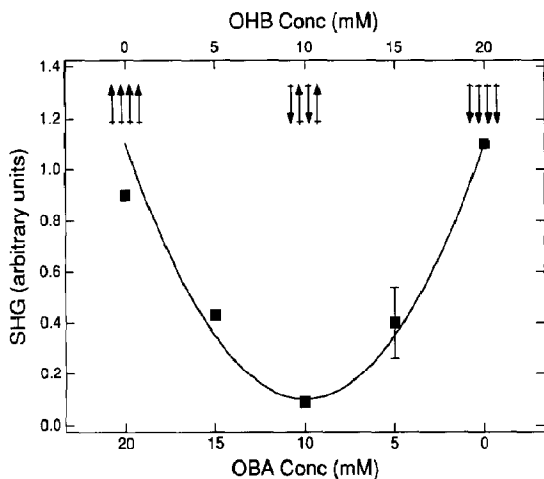

Fig. 4. SHG Intensity as a function of OBA and OHB concentration in the bulk DCE phase. The decrease in the SHG from the interface in the presence of coadsorbed OBA and OHB molecules indicates that the SHG from OBA is $\approx 180°$ out of phase with that from OHB. This interference effect verifies that the dipole moments of OBA and OHB are aligned in opposite directions, as shown in fig. 1. The interference pattern can be qualitatively fit (———) assuming a competitive Langmuir adsorption isotherm.

formed to further elucidate the effect of an externally applied potential on the molecular orientation within monolayers adsorbed at the ITIES.

Acknowledgement

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