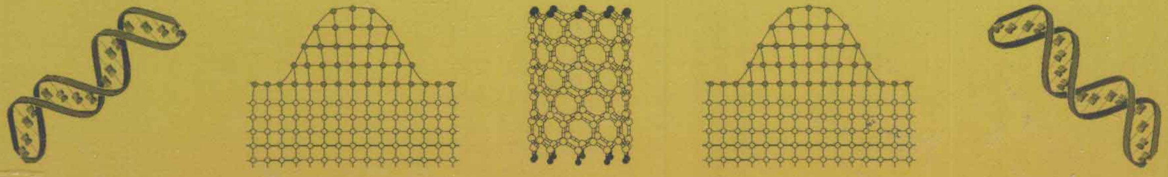

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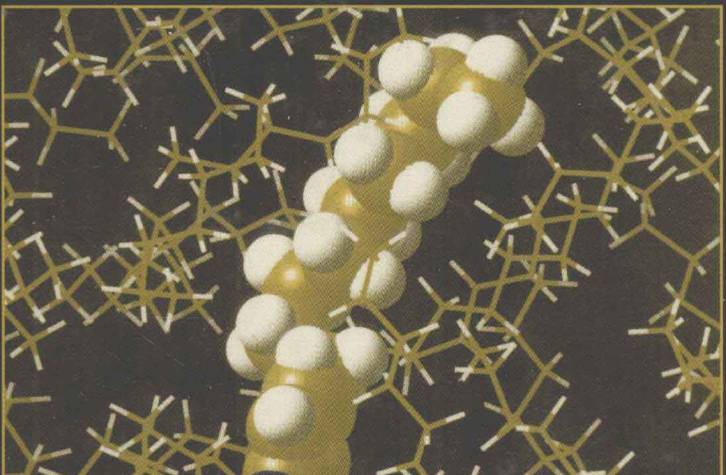
Interfacial Nanochemistry

Molecular Science and Engineering at Liquid–Liquid Interfaces



Edited by
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Preface

The history of the liquid–liquid interface on the earth might be as old as that of the liquid. It is plausible that the generation of the primitive cell membrane is responsible for an accidental advent of the oldest liquid interfaces, since various compounds can be concentrated by an adsorption at the interface. The presence of liquid–liquid interface means that real liquids are far from ideal liquids that must be miscible with any kinds of liquids and have no interface. Thus it can be said that the non-ideality of liquids might generate the liquid–liquid interface indeed and that biological systems might be generated from the non-ideal interface. The liquid–liquid interface has been, therefore, studied as a model of biological membrane.

From pairing two-phases of gas, liquid and solid, nine different pairs can be obtained, which include three homo-pairs of gas–gas, liquid–liquid and solid–solid pairs. The gas-gas interface, however, is practically no use under the ordinary conditions. Among the interfaces produced by the pairing, the liquid–liquid interface is most slippery and difficult to be studied experimentally in comparison with the gas–liquid and solid–liquid interfaces, as the liquid–liquid interface is flexible, thin and buried between bulk liquid phases. Therefore, in order to study the liquid–liquid interface, the invention of innovative measurement methods has a primary importance.

At the liquid–liquid interface, completely different properties of water and organic phases can be met in the two-dimensional boundary with a thickness of only 1 nm. In practical two-phase systems with highly miscible components, however, the formation of nano- and micro-droplets at the interfacial nano-region is suggested. The structural and dynamic properties of molecules at the interface are the most important subject in the study of physics and chemistry at the interface. The solution theory of the liquid–liquid interface has not been established yet, though the molecular dynamics simulations have been developed as a useful tool for depicting the molecular picture of the solvent and solute molecules in the interfacial region.

The adsorption of reactant molecules at the interface significantly affects the overall reaction rate in the two-phase system by the catalytic function of the interface. The liquid–liquid interface itself is a unique catalyst with such a flexible adsorbed area, which can be expanded or shrunk easily only by stirring or shaking. The increase of the adsorbed reactant molecules results in the promotion of reaction rate and the product will be extracted into the organic phase depending on its hydrophobicity.

The accumulation of solute molecule at the interface is ready to produce assemblies or aggregates at the interface with somewhat oriented structure. Molecular network and two-dimensionally stacked compound can be produced at the interface. These aggregates exhibit molecular recognizing ability very often. Studies of these functions are very important to understand the role of biological membrane and protein–interface interaction at the membrane.

This book is intended to make clear the front of the state-of-the art of the nanochemistry of the liquid–liquid interface. The plan to make this book had started from the discussion with Mr. Kenneth Howell of Kluwer Academic Publishers just after the Symposium on "Nano-Chemistry in Liquid–Liquid Interfaces" at the Pacifichem 2001 held in Hawaii. In the year of 2001, the Scientific Research on Priority Areas "Nano-Chemistry at the Liquid–Liquid Interfaces" (2001–2003) was approved by the Ministry of Education, Culture, Sports, Science and Technology of Japan. So, it will be timely to review some important studies accomplished in the project and to learn more about the liquid–liquid interfacial science by inviting outstanding researchers through the world as authors.

The title of this book is Interfacial Nanochemistry, but almost all the chapters are devoted to the research of the liquid–liquid interface and the unique chemistry at the interface. In spite of its being the most important interface for our biological world, we have the least knowledge about it. It might be our great pleasure if our readers could find any new concepts on the physical and chemical functions of the liquid–liquid interface in this book. I sincerely wish readers to improve their knowledge on the liquid–liquid interface and to produce any new ideas for the research or application of the liquid–liquid interface.

I would like to express my sincere thanks to the authors for submitting their worthy accomplishment and to the members of the Scientific Research of Priority Areas "Nano-Chemistry at the Liquid–Liquid Interfaces" for cooperating to build the new field of Interfacial Nanochemistry. I am deeply indebted to Dr. Hideo Akaiwa, a president of Gunma University, and Professor Fumiyuki Nakashio of Sojyo University for the success in our project. I also thank Mr. Kenneth Howell for his kind encouragement to produce this book, and Ms. Keiko Kaihatsu for her efforts on editing the manuscripts. This work was in part supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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Contents

1

Second Harmonic Generation at Liquid/Liquid Interfaces

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1.1. INTRODUCTION

Processes occurring at the interface between two immiscible liquids underlie many important phenomena in chemistry and biology, including liquid extraction, liquid chromatography, phase transfer catalysis, membrane processes and drug delivery. Understanding the role of structure and dynamics of these interfaces on adsorption to, solvation at and transfer across the interface is of direct relevance to these physicochemical processes. The study of such interfaces by macroscopic measurements such as surface tension while yielding significant information on the interfacial properties cannot yield microscopic or molecular detail. The non-linear optical techniques of second harmonic generation (SHG) and sum frequency generation (SFG) have been useful in probing the liquid/liquid interface.

SHG is a coherent process and in principle the experimental system needed to observe the response is very simple. The fundamental radiation from a laser source incident at an interface generates the harmonic beam via non-linear polarization of the medium. Typically, this beam is observed in reflection, but many studies have been undertaken in total internal reflection and transmission geometries. As the harmonic beam is well separated from the fundamental in frequency, it can be detected; the difficulties arise due to the inherent inefficiency of the harmonic generation and the low intensities that need to be detected. The sensitivity and selectivity of SHG to the interfacial species in the presence of the same species in the bulk phase provides the driving force to overcome these experimental difficulties.

There are several reviews of interfacial SHG which cover the theory and applications of SHG in general and describe some applications to the liquid/liquid interface [1–5]. In particular, the chapter by Brevet and Girault on Second Harmonic Generation at

Liquid/Liquid Interfaces [6] is an excellent discussion of the topic. In this review I will focus on a number of different examples of the application of SHG to liquid/liquid studies mainly from my own research group.

1.2. SHG THEORY

The SHG signals arise from the second-order polarization $\mathbf{P}^{(2)}$ induced in a non-centrosymmetric medium by the electric field $\mathbf{E}(\omega)$ of the incident fundamental radiation given by the tensor equation

$$\mathbf{P}^{(2)}(\omega) = \varepsilon_0 \chi^{(2)} \mathbf{E}(\omega) \mathbf{E}(\omega) \tag{1}$$

where $\chi^{(2)}_{ijk}$ is the third rank tensor expressing the second-order surface susceptibility of the material. In a centrosymmetric medium, no second-order polarization is possible in the dipole approximation. At an interface, the inversion symmetry is broken and a dipole contribution to $\mathbf{P}^{(2)}$ is allowed. The polarization at the interface is usually treated as a sheet of thickness much smaller than the wavelength of light. This polarized sheet gives rise to the harmonic wave generated in reflection or transmission, with the propagation directions being defined by conservation of momentum.

Equation (1) does hide some of the complexities as it emphasizes the local response, but the non-local terms can be significant and, for example, higher order quadroplar terms and terms involving the electric field gradient or magnetic terms lead to contributions to the SHG signal from the bulk. These terms all involve a derivative of the electric field vector. For most materials the magnetic terms are not significant and the electric quadrupole term provides the main contribution from the bulk. If SHG studies are extended to ferroelectric fluids, the magnetic term may need to be included.

The intensity $I(2\omega)$ of the SHG signal observed from an interface between two isotropic bulk phases illuminated with fundamental radiation of intensity $I(\omega)$ is given by [7]

$$I(2\omega) = \frac{32\pi^3\omega^2}{c^2} \frac{\sqrt{\varepsilon_1(2\omega)}}{\varepsilon_1(\omega)\left(\varepsilon(2\omega) - \varepsilon_1(2\omega)\sin^2\theta_1(2\omega)\right)} \tag{2}$$
$$|\mathbf{e}(2\omega)\cdot\chi^{(2)}\cdot\mathbf{e}(\omega)\mathbf{e}(\omega)|^2 I^2(\omega)$$

where $\mathbf{e}(\omega)$ and $\mathbf{e}(2\omega)$ are the polarization vectors for the fundamental and harmonic beams and include the appropriate combination of Fresnel factors. The refractive indices and permittivities ε_i, are defined for each layer of the three-layer model (Figure 1.1) and θ_1 is the angle of reflection of the harmonic beam in the upper layer. As written, Equation (2) applies when the permittivities are real and a more general expression is given by Brevet [7]. As explained by Brevet (chapter 7), for the three-layer model it is the real parts of the permittivity that are significant for the leading terms in Equation (2), though the full complex quantities are involved in the calculation of the Fresnel factors.

For an isotropic (in-plane) interface, only four of the tensor components, χ_{ZZZ}, χ_{ZXX}, χ_{XZX} and χ_{XYZ} where Z is the normal to the interface, contribute to the observed harmonic signal. The electric field of the S($E^{\mathrm{S}}_{2\omega}$) and P($E^{\mathrm{P}}_{2\omega}$) polarized components of the harmonic beam as a function of the linear polarization angle (γ) of the fundamental

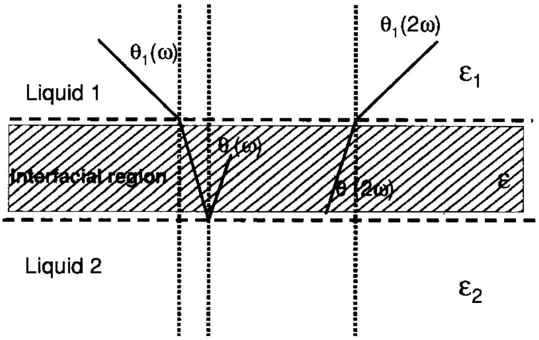

FIGURE 1.1. Layer model with the permittivity associated with each layer. The upper bulk phase is region 1 and the lower bulk phase surrounding the interface is region 2. The interface is considered as a microscopically thin region between the two bulk phases. In general, for a liquid/liquid or liquid/solid interface, dispersion may be significant and the reflection angle for the harmonic will differ slightly from the angle of incidence of the fundamental.

wave (assuming a pure linear polarization) are given by

$$E^{\mathrm{S}}_{2\omega} = S\left(a_1\chi_{XZX}\sin 2\gamma + a_6\chi_{XYZ}\cos^2\gamma\right) \tag{3}$$

$$E^{\mathrm{P}}_{2\omega} = S\begin{pmatrix}(a_2\chi_{XZX} + a_3\chi_{ZXX} + a_4\chi_{ZZZ})\cos^2\gamma + \\ a_5\chi_{ZXX}\sin^2\gamma - a_7\chi_{XYZ}\sin 2\gamma\end{pmatrix} \tag{4}$$

The χ_{XYZ} component is only non-zero for chiral surfaces; the value of χ_{XYZ} for two enantiomers will be equal in magnitude but opposite in sign. As the tensor components can be complex quantities (especially near resonance), the harmonic wave can be elliptically polarized even for a linearly polarized fundamental, just as in conventional ellipsometry. This results in a variety of interesting effects of non-linear optical activity being observable in SHG [8–13]. The majority of observations of this type have been made on chiral films [14,15].

The a_i coefficients are combinations of Fresnel factors relating the electric fields in the interfacial region to the external field and they depend on the exact model for the interface chosen. For the second harmonic calculations, a simple three-layer model (Figure 1.1) is typically used. The non-linear region is the thin layer between bulk immersion medium layers. It is important to realize that this layer is assumed always to be vanishing thin, being on the order of the molecular dimension of the target, because thicker assemblies of molecules are usually centrosymmetric and do not generate even harmonics. The second harmonic calculations therefore assume that there is no significant light interference in this layer, although there is reflection at its upper and lower boundaries. This is in contrast to macroscopic layered structures often investigated by linear ellipsometry, where interference effects within the layer can contribute dominantly to the overall polarization changes.

In the absence of chiral effects it is often convenient to fit the polarization data, in the first instance, to the phenomenological equations (5) and (6) that describe the expected shape of the polarization behaviour [16]. For the P-polarized harmonic intensity, I_{P} is given by

$$I_P = |A\cos^2\gamma + B\sin^2\gamma|^2 \tag{5}$$

and for the S-polarized harmonic intensity, I_S is given by

$$I_S = |C\sin 2\gamma|^2 \tag{6}$$

where $\gamma = 0°$ corresponds to P-polarized and $\gamma = 90°$ to S-polarized fundamental fields. The parameters A, B and C, *which may be complex*, are linear combinations of the components of the second-order susceptibility, χ tensor, and the non-linear Fresnel coefficients, a_i, This allows the initial model to be fit without the concern of the often unknown interfacial refractive index that is required to evaluate the Fresnel coefficients, a_i. More details of this procedure and the model-dependent assumptions used in the data analysis are discussed later.

The additional terms that need to account for the main non-local effects include the effects of the field gradient at the interface. Following Brevet [7] we can write

$$\mathbf{P}^{(2)} = \chi^s\mathbf{EE} + \gamma\nabla[\mathbf{EE}] - \nabla[\chi_Q]\mathbf{EE} \tag{7}$$

Fortunately these terms can be cast into the same form as the surface dipole susceptibility giving effective surface tensor components which are given by

$$\begin{aligned}\chi_{XXZ}^{\text{interface}} &= \chi_{XXZ}^{\text{s}} + \chi_{XXZ}^{\text{eff}} \\ &= \chi_{XXZ}^{\text{s}} + \chi_{ZXXZ}^{\text{Q1}}\frac{\varepsilon(\omega)}{\varepsilon_1(\omega)} - \chi_{ZXXZ}^{\text{Q2}}\frac{\varepsilon(\omega)}{\varepsilon_2(\omega)}\end{aligned} \tag{8}$$

$$\begin{aligned}\chi_{XZX}^{\text{interface}} &= \chi_{XZX}^{\text{s}} + \chi_{XZX}^{\text{eff}} \\ &= \chi_{XZX}^{\text{s}} + \chi_{ZXZX}^{\text{Q1}}\frac{\varepsilon(\omega)}{\varepsilon_1(\omega)} - \chi_{ZXZX}^{\text{Q2}}\frac{\varepsilon(\omega)}{\varepsilon_2(\omega)}\end{aligned} \tag{9}$$

$$\begin{aligned}\chi_{ZXX}^{\text{interface}} &= \chi_{ZXX}^{\text{s}} + \chi_{ZXX}^{\text{eff}} \\ &= \chi_{ZXX}^{\text{s}} + \left(\gamma_1 + \chi_{ZZXX}^{\text{Q1}}\right)\frac{\varepsilon(\omega)}{\varepsilon_1(\omega)} - \left(\gamma_2 + \chi_{ZZXX}^{\text{Q2}}\right)\frac{\varepsilon(\omega)}{\varepsilon_2(\omega)}\end{aligned} \tag{10}$$

where the superscript s specifically indicates the dipole surface terms and eff the effective surface contribution of the bulk quadruple and gradient terms.

As pointed out by Brevet and Girault [17], this analysis shows that the discussion of SHG data from liquid/liquid interfaces must be cognisant of the possible contributions from the bulk and from field gradients at the interface. However, in the liquid/liquid case, the changes in optical constants from one bulk phase to the other will normally be less marked than that observed in air/liquid experiments. Of course in the limit of the same optical constants for the two phases, there would be no gradient effects but there would also be no reflection.

In order to extract information on the molecular orientation distribution, the relationship between the macroscopic surface susceptibilities and the molecular hyperpolarizabilities, β, needs to be considered. It is usual to consider the intrinsic non-linear response of each of the molecules as independent of the other molecules so that the interfacial response is an average over the orientational distribution and scales with the molecular density (squared). Even the modification of this response due to local field effects is usually considered in terms of mean field model and so does not alter the nature of this averaging (three additional diagonal terms need to be included).

$$\chi = \mathbf{T}\{N\langle\beta\rangle\} \tag{11}$$

where N is the surface number density and < > represents the average over the orientational distribution. The transformation between the molecular axis system (ijk) and the interfacial coordinate system (IJK) involves the various direction cosines, and the tensors involved are both third rank three rotation matrix terms, **R**, are present [18–20].

$$\chi_{IJK} = N\left\langle \sum\sum\sum R_{Ii}R_{Jj}R_{Kk}\beta_{ijk}\right\rangle \tag{12}$$

In many cases it is possible to simplify these equations because only relatively few components of β are significant, either because of the symmetry or the electronic structure of the molecules. When it is possible to reduce the number of distinct significant components to at most two, then it is often possible to extract the ratio of these components and geometric information directly from the observed values of the susceptibility. In these cases the values assumed for the interfacial refractive index and the role of the contributions from the bulk can make a dramatic difference to the derived geometric parameters [21–27].

While some qualitative inferences about the nature of the interface can be derived directly from the SHG observations, extracting detailed quantitative information from the SHG intensity and polarization data requires the construction of a model of the interface and frequently assumptions about some of the parameters for this model. Parameters such as the interfacial refractive index and roughness need to be determined separately, calculated or more frequently obtained by reasonable assumptions [20,21,23–27]. Some idea of the relationship between the model, assumptions and results is given in Figure 1.2.

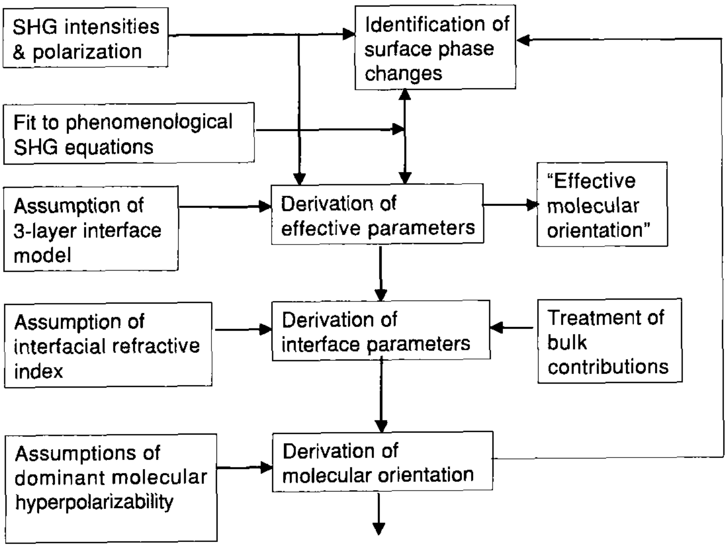

FIGURE 1.2. A guide to the modelling and assumptions needed to interpret the SHG intensity and polarization data.