STUDIES OF MOLECULAR PROPERTIES AT THE SURFACE OF A LIQUID JET BY SECOND HARMONIC GENERATION

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We report the use of second harmonic generation (SHG) to study kinetics of adsorption of *p*-nitrophenol at the air/water interface of a flowing jet. Measurements of the SH signal strength and the polarization of the SH light at various distances (times) along the jet axis yield information about the development of the population density and orientation of nitrophenol at the air/water interface. The kinetics of adsorption are consistent with the Langmuir theory. The free energy of adsorption obtained from the jet experiments was the same as that obtained from static experiments. The orientation of nitrophenol at the jet air/solution interface was the same as for the static (equilibrium) interface; orientational equilibrium is rapidly achieved.

1. Introduction

From the results of a rapidly increasing number of studies we see that second harmonic (SHG) and sum frequency generation (SFG) are powerful methods to study a variety of interfaces [1–9]. The increasing importance of SHG and the related process of SFG is due to the interfacial selectivity of these techniques, which derives from the fact that they are electric dipole forbidden in centrosymmetric media. Since the symmetry is broken at the boundary between two centrosymmetric media, it follows that SHG can be used to selectively probe the interfacial region. In this laboratory, information about the relative populations, molecular energetics and chemical dynamics of various molecules at the air/water interface have been obtained using this method [10–14].

In this paper we wish to report the use of surface second harmonic generation to study molecular equilibrium and dynamic processes at the surface of a liquid water jet. The use of a liquid jet is a potentially important way to study interfaces in that it permits the study of equilibrium, e.g., orientational structure and solute adsorption energetics, as well as dynamic molecular processes in systems where the interfering effects of irreversible photochemical and thermal processes can be minimized or avoided by

the continuously generated fresh surface. It also offers the possibility of generating desired nonequilibrium populations at an air/liquid interface by controlling the characteristics of the solid/liquid interface of the nozzle immediately prior to the formation of the jet. In this study, it is the dynamics of the adsorption of an organic molecule, *p*-nitrophenol, to the air/water jet interface that we report.

The initial population density of nitrophenol molecules at the liquid interface that exit the glass nozzle is determined by the nitrophenol interactions at the glass/water interface, not its interactions at the later developing air/water jet interface. Thus, the air/water jet interface has a surface density of nitrophenol molecules that initially is not its equilibrium value. The experiments measure the time it takes the interface to achieve its equilibrium physical and chemical state. From our determination of the jet velocity we know the elapsed time from the jet nozzle to each position along the axis of the jet. The time-dependent change in the nitrophenol population at the air/water jet interface can therefore be obtained by measurement of the SH signals at various distances from the jet nozzle. We take the square root of the SH signal, since for a coherent process this is the quantity that is proportional to the number of nitrophenol molecules/cm² at the interface. For purposes of comparison, we note that dynamic surface

tension and surface potential methods have been used to measure some surface equilibration times [15–17]. However, they lack the selectivity to probe specific molecules at the interface, characteristics that are inherent in the laser pulse spectroscopic SH technique.

2. Experimental results

In the present study, measurements of the SH signal strength and the polarization of the SH light at various distances (times) along the jet axis yield information about the population and orientation of nitrophenol at the air/water interface. The laser system used in these experiments was a synchronously pumped cavity-dumped picosecond dye laser operating at 610 nm and providing 5 ps pulses at 4.1 MHz. The laser beam was focused down to 10 μm at the surface of the sample. For the static measurements, the liquid sample was contained in a 10 ml beaker. For the dynamic experiments, the liquid sample flowed through a tubular glass nozzle constricted at the end such that a liquid jet of circular cross section and 2 mm diameter was obtained. Laminar flow was achieved by circulating the liquid at 340 ml/min and 10 psi, yielding an optically flat jet surface with a velocity of 180 cm/s. The glass nozzle was positioned parallel to the optical table and perpendicular to the plane of incidence. The laser beam was reflected off the jet surface at an angle of 70°. The reflected second harmonic light at 305 nm was directed through an analyzer, monochromator, cooled PMT and single photon counting electronics. The pH of the p-nitrophenol/water solution was 2, at which value the protonated form predominates in the bulk ($pK_a = 7.2$) and interface [10]. p-nitrophenol was obtained from Aldrich (99+%) and recrystallized before use. HPLC grade water (Aldrich) was used as received. For experiments with an ethylene glycol jet, which will be reported in a later publication, a standard dye laser nozzle was used to obtain an optically flat air/solution interface.

Second harmonic s-polarized amplitudes were obtained for p-nitrophenol solutions with concentrations from 5 to 100 mM. The distance from the nozzle tip to the laser spot was varied from 1 to 40 mm, which correspond to times of 0.55 to 22.0 ms. Sec-

ond harmonic experiments were also performed over the same concentration range, on the air/water interface of a static cell. The static interface experiment yields the equilibrium adsorption isotherm of nitrophenol to the air/water interface. The small background due to water was subtracted out. Fig. 1 shows the p-nitrophenol SH electric field, $E_{2\omega}^s$, plotted against time. Only three concentrations are shown for clarity. The rest of the data shows the same trend of adsorption increment with time. No leveling off was detected for any concentration, which means that p-nitrophenol requires more than 22 ms to reach its final adsorption equilibrium. The fraction of the equilibrium value reached at this longest measurement time is 88%, 67% and 41% for the respective concentrations of 67, 33 and 10 mM.

3. Discussion

3.1. Time-dependent Langmuir model

Comparison of the time-dependent SH data with the predictions of the Langmuir model [18] shows that this model is consistent with the dynamic behavior of p-nitrophenol at the air/solution interface of a liquid jet. The Langmuir model assumes that the surface can be treated as a lattice of non-interacting sites, and that the adsorption process can be described by the "reaction" between bulk molecules
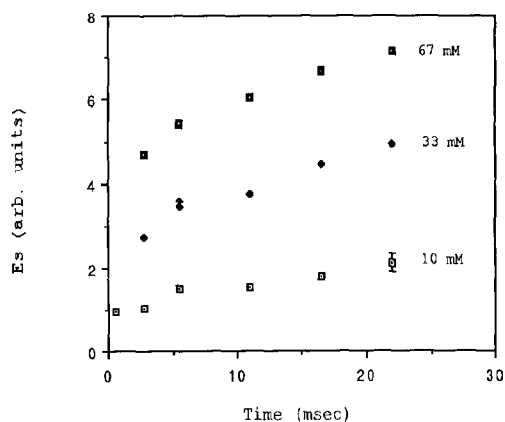

Fig. 1. Surface second harmonic electric field, $E_{2\omega}^s$, as a function of time for three different concentrations of p-nitrophenol.

(M) and empty surface sites (ES) to give filled sites (FS):

$$M + ES \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FS .\qquad(1)$$

The kinetic equation is

$$\frac{dN}{dt} = k_1 x (N_{max} - N) - k_2 N ,\qquad(2)$$

where N is the number of adsorbed molecules/cm^2, N_{max} its maximum value, k_1 and k_2 the rate constants for adsorption and desorption, respectively, $x = C/55.5$ the bulk mole fraction, C the bulk concentration and 55.5 the molarity of water. By setting $dN/dt = 0$, one obtains the equilibrium Langmuir equation, $N_e/N_{max} = k_1 x / (k_1 x + k_2)$. Substituting the expression for N_{max} from this relation into (2) and integrating, one obtains

$$\ln(N_e - N) = -(k_1 x + k_2) t + \ln(N_e - N_0) ,\qquad(3)$$

where $\ln(N_e - N_0)$ is the integration constant, which appears by setting $N = N_0$ at $t = 0$. We can test the applicability of the Langmuir model by plotting $\ln(N_e - N)$ versus time for each concentration, noting that the SH electric field is proportional to N, and N_e is obtained by measurement of a static (equilibrium) interface. We should obtain a straight line with slope $-(k_1 x + k_2)$ if the Langmuir model is applicable. We see in fig. 2 for $C = 67$ mM, and for the other concentrations not shown, that the linear de-
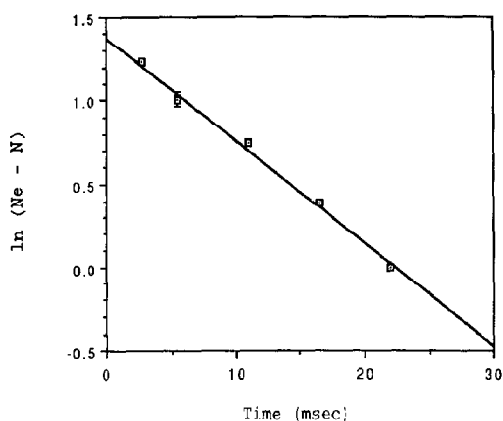
pendence on time predicted by the model is obeyed. Finally, by plotting $k_1(C/55.5) + k_2$ versus C (fig. 3), the rate constants k_1 and k_2 can be found. The values obtained are $k_1 = (4.4 \pm 0.2) \times 10^4$ s^{-1}, $k_2 = 6 \pm 2$ s^{-1}, and $\Delta G^0_{jet} = -RT \ln(k_1/k_2) = -5.1 \pm 0.2$ kcal/mol. The large difference in the values of k_1 and k_2 can be explained in terms of the relative energy barriers for adsorption and desorption. The adsorption process requires the replacement of water by a nitrophenol molecule, which lowers the surface free energy, whereas desorption requires the immersion of the hydrophobic phenyl group into the bulk; the latter process is less favorable than the former. Thus, the equilibrium is strongly displaced toward the formation of filled sites ($K = k_1/k_2 \approx 7300$), as indicated by the relatively large negative value of ΔG^0 for the adsorption "reaction" given by eq. (1). In the static experiment, the free energy of adsorption was calculated from the equilibrium Langmuir isotherm [19]. The value obtained for the static cell, $\Delta G^0 = -5.15 \pm 0.02$ is in excellent agreement with the value obtained from the jet experiments, thus indicating that the Langmuir kinetic theory is consistent with the dynamic adsorption of p-nitrophenol at the air/solution interface. It is interesting to note that N_0, the concentration of nitrophenol at $t = 0$, can be obtained from the intercept of eq. (3). This initial population of nitrophenol at the jet air/water interface is determined by the concentration at the glass/
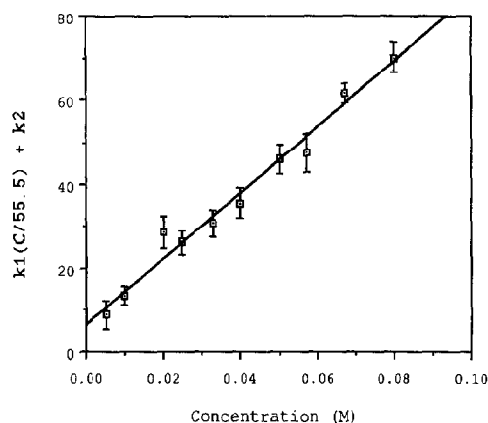

Fig. 2. $\ln(N_e - N)$ versus t for $C = 67$ mM (see eq. (3)). N_e is the equilibrium surface concentration (molecules/cm^2) and N is the surface concentration at time t after leaving the nozzle.

Fig. 3. $k_1(C/55.5) + k_2$ versus concentration. The rate constants k_1 for adsorption and k_2 for desorption were obtained from the slope and intercept, respectively. C is the bulk concentration of p-nitrophenol in mol/ℓ and 55.5 is the molarity of H$_2$O.
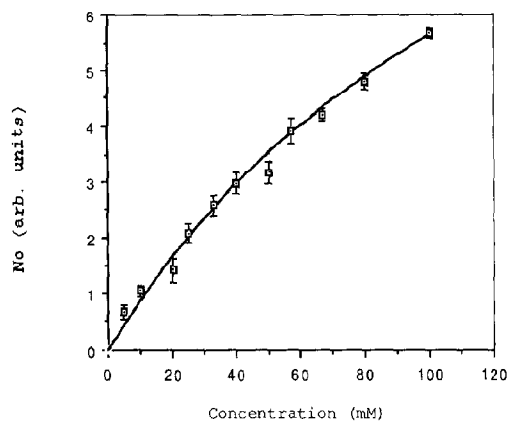
Fig. 4. N_0 versus C. The solid line represents the best fit to the Langmuir equation. N_0 is the surface concentration at $t=0$, C is the bulk concentration.

water interface. Thus, information about the adsorption at the glass/water interface can be obtained from N_0. As can be seen from fig. 4, our experimental N_0 values show a Langmuir-type dependence on concentration, indicating that adsorption to the glass/water interface follows the Langmuir model as well. The value obtained, $\Delta G^0 = -3.4$ kcal/mol at the glass/water interface is less negative than that obtained for the air/water interface. This lower value at the glass/water interface is related to the higher surface free energy of the air/water interface than the glass/water interface. There is a larger reduction in hydrophobic interactions for p-nitrophenol at the air/water interface than at the hydrophilic glass/water interface. Further experiments on the direct measurement of SH signals at the glass/water interface are in progress.

3.2. Solute diffusion to the interface

To determine the role of diffusion in the adsorption process, our data were compared to a simple diffusion theory [20,21]. At early times or low concentrations, the following equation yields the solute interface concentration at time t:

$$dN(t)/dt = (D/\pi)^{1/2}Ct^{-1/2}(N_A/1000) \tag{4}$$

and therefore

$$N(t) = 2(D/\pi)^{1/2}Ct^{1/2}(N_A/1000) + N_0 , \tag{5}$$

where D is the diffusion coefficient in cm²/s and N_A is Avogadro's number. Our experimental values of nitrophenol at the air/water interface $N(t)$ at time t do not give a good fit to the $t^{1/2}$ dependence. In the best cases, the values of D obtained (10^{-10}–10^{-11} cm²/s) are physically unrealistic for organic molecules in water. Furthermore, for a diffusion-controlled process, the rate constant k_1 would be time dependent, as can be seen from eq. (4), which is consistent with the linearity of the plot shown in fig. 3. These observations indicate that diffusion is not the rate-limiting step, and that the kinetics of adsorption is determined by a barrier crossing. We can make a rough estimate of the barrier height by calculating the adsorption kinetics for a diffusion model and comparing it with the kinetics that fit our data. The kinetics which describes our observations for the adsorption step is given by eq. (3), with k_2 set equal to zero. We set $k_2 = 0$ because we are only comparing the adsorption part of the kinetics for the two cases. We calculate the time it takes $(N_e - N)/(N_e - N_0)$ to reach the value of $1/e$. This time τ is related to the time it takes N to reach $1/e$ of its equilibrium value starting at an initial value of N_0. For the barrier model, i.e. the one that fits our data, we use eq. (3), with $k_2 = 0$. The time τ is equal to $55.5/k_1C$ for this case and ranges in value from 13 to 260 ms for the different bulk concentrations used. For the diffusion case we use eq. (5) and for the same bulk concentrations as above, we find that the time τ it takes $(N_e - N)/(N_e - N_0)$ to reach $1/e$ ranges from 7 µs to 3 ms. It is therefore seen that the experimental adsorption times are considerably longer than those obtained if diffusion alone was responsible for the kinetics of adsorption. To estimate the barrier height, we assume an Arrhenius-type relationship between τ^{diff} and τ^{barr}:

$$\tau^{\text{diff}} = \tau^{\text{barr}} \exp(-E^*/RT) . \tag{6}$$

The values obtained in this way for the barrier height E^* are in the range of 3–4 kcal/mol.

3.3. Orientational equilibration at the interface

Since the polarization of the SH light has been found to be the same for the static cell and jet, we conclude that the orientation of nitrophenol is the same for both cases. This means that the nitrophenol

molecules have achieved the equilibrium orientational distribution at our earliest measurement time of 0.55 ms. This is consistent with the fact that the reorientation time for organic molecules is expected to be much faster than this; in bulk solution it is of the order of 10^{-11} s. We therefore see that although the time required to achieve the equilibrium population is long, the nitrophenol molecules at the interface very rapidly achieve their equilibrium orientation. Similarly, for the case of neat water, we find the same polarization of the SH light for the jet and the static cell from 0.55 ms and longer, thus indicating that the orientation of the water at the interface is achieved rapidly and is the same for the stationary and moving interfaces.

4. Conclusions

In conclusion, we have generated second harmonic light from the surface of a liquid jet. Using this technique we have been able to study the kinetics and energetics of adsorption of p-nitrophenol to the air/water interface. We found that the adsorption kinetics to the liquid jet/air interface could be described by a dynamic Langmuir model. From the kinetics we obtained the rate constants of $(4.4 \pm 0.2) \times 10^4$ s^{-1} for adsorption and 6 ± 2 s^{-1} for desorption. The free energy of adsorption for the process was found to be $\Delta G_{ads}^0 = -5.1 \pm 0.2$ kcal/mol, which is the same as for the static (equilibrium) case. The kinetic data also yield the initial surface population of p-nitrophenol at the air/water interface, which thereby gives information about the adsorption at the preceding glass/water interface of the jet nozzle. For this interface, we found that $\Delta G^0 = -3.4$ kcal/mol. We also found that adsorption of p-nitrophenol to the air/water interface is considerably slower than diffusion controlled, thus indicating that the adsorption rate is kinetically controlled by a barrier. A rough estimate of the barrier hight yields a value of 3-4 kcal/mol. The orientation of nitrophenol at the liquid jet/air interface was the same as for the static (equilibrium) liquid/air interface, which indicates that orientational equilibrium was achieved prior to the earliest measurement time, 0.55 ms. In addition, we note that this method offers the possibility of generating various nonequilibrium populations of species at air/liquid interfaces and also opens the possibility of investigating static and dynamic interfacial processes by avoiding the interfering effects of irreversible photochemical and thermal processes common to many systems.

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