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"Total Internal Reflection Second Harmonic Generation from the Interface Between Two Immisicible Electrolyte Solutions"

by

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Total Internal Reflection Second Harmonic Generation from the Interface between Two Immisicible Electrolyte Solutions.

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Abstract.

Total internal reflection second harmonic generation (TIR SHG) is used to investigate the interface between two immiscible electrolyte solutions (ITIES) under potential control. The observed potential dependent second harmonic response is attributed to a resonance enhanced process arising from the tetraphenylborate (TPB^-) ion. As the aqueous phase is biased positive of the organic phase, a large increase in the SH response is observed and is attributed to the adsorption of the TPB^- ion at the interface. The potential dependent SH data allows for the determination of the TPB^- anion concentration at the interface. TIR SHG compliments measurements of the electrolyte surface excess and can function as a means of measuring the relative concentration of electrolytic species responsible for the potential drop across the electrochemical double layer.

I. Introduction.

The nature of the electrochemical interface between two immiscible electrolyte solutions (ITIES) or liquid/liquid interfaces has been studied extensively due to the central role these systems play in chemistry and biology. The transport of molecular and ionic species across a liquid/liquid phase boundary is dependent upon the structure of the interfacial region and the electrostatic and intermolecular forces therein. A detailed understanding of the structure and order of both solute and solvent molecules at the interface is needed to better understand adsorption and transport properties of such interfaces. The ITIES has been one of the most studied heterogeneous liquid systems involving mass transport.[1-6] Such systems have been investigated by a number of electrochemical, cyclic voltammetery, capacitance and electrocapillary measurements and from these studies the double layer structure of the ITIES has been inferred.[3, 7-12] However, a detailed spectroscopic investigation of the interfacial structure or absorption of solvent or solute molecules at the interface has never been made. There have been a number of spectroscopic investigations undertaken in order to ascertain the structure of these complex interfaces by monitoring the spectroscopic behavior of molecular surfactants adsorbed at the interface.[13-16] The presence of these surfactants however can significantly alter the native double-layer structure, allowing one to only speculate about the interfacial structure in the absence of a surfactant.

Although spectroscopic techniques hold the promise of being able to elucidate the underlying structure of these interfaces, there is the problem of isolating the response arising from the interface from that of the more pervasive bulk liquids. The method of optical second harmonic generation, an inherently surface specific technique, has the ability to probe the interfacial region without interference from the surrounding bulk liquids. Under the electric-dipole approximation, SHG is not allowed in the bulk of centrosymmetric media such as liquids.[17] At an interface, where the distribution of material in the two adjoining phases is discontinuous, the inversion symmetry of the bulk is broken and a nonlinear polarization can be induced. By applying an optical field of sufficient intensity at frequency ω, a second optical field is produced by the nonlinear polarization at frequency 2ω. If any of the species at the interface are resonant with the fundamental or second harmonic frequency, SHG can be used to determine the relative concentration of that species at the interface.[17] Because of this unique surface specificity, SHG has been exploited extensively to investigate a number of interfaces.[18-23]

In the studies to be described, optical second harmonic generation is used to study the n-alkane/water and water/1,2-dichloroethane (water/DCE) interfaces. The electrolytic water/DCE interface has also been examined and the SH response measured as a function of the applied potential. Although such experiments are difficult if not impossible to perform by SHG due to low signal levels, success in performing the studies described herein has come from using a unique total internal reflection (TIR) geometry to enhance the interfacial SH response.[24] With this geometry, a 10-100 fold increase in SHG is achievable as the incident angle approaches the critical angle. Such an increase in sensitivity has in turn lead to important insight into the relative ordering of different alkane/water systems.[25, 26] For the water/DCE electrolyte studies the potential dependent adsorption/desorption of the TPB^- ion has been monitored.

II. Experimental.

For the electrochemical SH measurements, HPLC grade 1,2-dichloroethane (DCE) obtained from Aldrich and water obtained from a NANOpure II water purification system with a measured resistivity of 17.8 Mohm-cm were used. The supporting electrolytes, lithium chloride (LiCl), tetrabutylammonium tetraphenylborate (TBATPB) and tetrabutylammonium chloride hydrate (TBACl) were purchased from Aldrich and used as received. The electrochemical and SH measurements were performed with 1.0 mM aqueous solutions of LiCl and TBACl. TBATPB (1.0 mM) was used as the supporting electrolyte in the DCE. The aqueous LiCl and organic solution of TBATPB were equilibrated by shaking the solutions together prior to use. All solvents were filtered through a 0.5 μm Teflon filter to use to remove any particulates.

Electrochemical measurements were performed with a JAS Instruments model J-1600-B four electrode potentiostat and a model JJ1276 waveform programmer. Platinum wire coils were used as counter electrodes in the aqueous and organic phases and placed directly above and below the interface. Ag/AgCl reference electrodes were used for both the aqueous and organic phases. The Ag/AgCl reference electrodes were housed in Luggin capillaries in both the aqueous and organic phases to reduce the potential drop due to the high solution resistance. The Luggin capillaries in the organic phase housed the Ag/AgCl reference electrodes in contact with an aqueous solution of 1.0 mM TBACl. The 1.0 mM TBACl solution serves as a junction between the Ag/AgCl reference electrode and the organic phase electrolyte solution. The resulting cell configuration is described schematically as:

$$\mathrm{Ag|AgCl \mid 1mM\ TBCl_{(aq)} \mid 1mM\ TBATPB_{(DCE)} \mid 1\ mM\ LiCl_{(aq)} \mid AgCl|Ag}$$

The interface between the 1.0 mM aqueous TBACl and 1.0 mM TBATPB solution which occurs just inside the Luggin capillary is non-polarizable with the potential drop across the interface being determined by the TBA^+ ion. The Ag/AgCl reference electrode, left hand side, in contact with the aqueous TBACl solution, effectively functions as a reference electrode reversible to TBA^+ ion. The Ag/AgCl reference electrode in the aqueous LiCl phase is reversible to Cl^- ion. The applied potential to the cell E_{app} is defined as the potential in the aqueous phase (w) minus the potential in the organic phase (o), $E_{app} = E_w - E_o$.[9, 12]

The optical second harmonic measurements were performed in a cylindrical quartz cell which houses the reference and counter electrodes (Figure 1). The optical cell was open to the atmosphere to avoid changes in the interfacial tension due to thermal fluctuations. The optical experiments were performed with the 532nm SH output of a Quanta-Ray DCR11 Nd:YAG laser. Pulses of 10ns duration and 2-5mJ at a repetition rate of 15 Hz were employed. The 532nm incident beam was collimated to a diameter of 0.25-0.5 mm and directed onto the interface from the 1,2-dichloroethane side of the interface. The input polarization was controlled by a halfwave plate. The transmitted SH response at 266nm was passed through a series of absorptive and interference filters to remove any residual 532nm light. The generated SH light was polarization selected and detected with a PMT. Gated electronics were used for SH signal collection.

Optical absorption spectra were collected with a Perkin Elmer Lambda 6 spectrophotometer. For all spectra collected a 1 cm path length quartz cell was used. For the 1,2-dichloroethane spectra a water reference was used. Acetonitrile was used as a reference for the spectra of 0.1mM TBATPB in acetonitrile.

III. Results and Discussion.

The second harmonic signal from liquid/liquid interfaces such as the ITIES examined here, is often too low to be detected. This is a consequence of the dynamic nature of the interface and the fact that liquids, in particular water and 1,2-dichloroethane, have relatively low polarizabilities. However, by using a total internal reflection (TIR) geometry, Conboy et al. have detected a considerable SH signal from a series of n-alkane/water interfaces.[25, 26] To demonstrate this point, the dependence of the SH response on the incident angle of the fundamental light source at frequency ω is shown for the decane/water interface (Figure 2a). As the incident angle approaches the critical angle (72°), the second harmonic response increases dramatically as seen in Figure 2a. The fundamental light (ω) at 532nm is incident upon the interface from the alkane side which possesses the higher index of refraction and the SH light (2ω) at 266nm is collected in reflection. The solid lines of Figure 2(a and b) represent the theoretically calculated SH intensity using a single adjustable parameter.[24-26] The two maxima displayed in the theoretical and SH intensities are due to the TIR of the fundamental and SH at their respective critical angles; for decane/water the angles are 70.6° and 75.7°.

Due to dispersion, a transmitted as well as a reflected SH field is produced by the nonlinear polarization induced at the interface, even when the fundamental is under total internal reflection.[24] The frequency dependent refractive indices of the liquids results in the SH at 2ω achieving TIR at an incidence angle larger than the critical angle of the fundamental at ω. The enhancement obtained under TIR for the reflected SH field has also been shown to hold for the transmitted SH.[24] The transmitted SH response shows the same dramatic increase over a very small incident angle distribution as a result of the TIR of the fundamental field. The SH signal disappears abruptly at an incident angle of 72° as the transmitted SH component becomes totally internally reflected. This technique has been applied to the neat water/1,2-dichloroethane interface as seen in Figure 2b. The 532nm light is propagated through the DCE and is reflected. The transmitted SH is propagated through the water and collected in transmission. Results are shown for the P_{in}/P_{out} polarization combination in Figure 2(a and b). This optical geometry is critical for measuring the SH response from the electrochemical interface or ITIES composed of an aqueous phase of LiCl and an organic phase of TBATPB in DCE. Both the DCE and TBATPB absorb at 266nm, as seen in their respective absorption spectra (Figure 3). Measurement of the SH response cannot be performed in reflection due to the high absorptivity in the organic phase. However, due to the symmetric nature of the induced SH field, the SH light propagated in transmission can be used. The strong absorption of the electrolyte TBATPB has additional implications for the observed SH signal. This will be discussed in further detail later as it pertains to the potential dependent SH response from the 1.0 mM LiCl, H_20/ 1.0 mM TBATPB, DCE interface.

Using the technique introduced above, the potential dependent SH signal for the ITIES composed of 1.0 mM LiCl, aqueous and 1.0 mM TBATPB in DCE was obtained.

The results are shown in Figure 4 and the corresponding cyclic voltammogram (CV) is displayed in Figure 5. Both sets of data were taken with potential limits of 100 mV to 520 mV and a scan rate of 5mV/sec. There is a potential window of 200mV from 0.200-0.400V under which the interface is ideally polarizable as seen by the negligible current flow in this region. Outside of this potential region, a large current is measured for potentials greater than 400mV and less than 100mV. Using the conventions previously established, the transfer of a positive charge from the aqueous to the organic phase is taken as the positive direction of the current flow.[12] The SH data shown in Figure 4 was collected at a fundamental incident angle of 67° and the SH signal was collected in transmission at an angle of 76°. The SH data was collected for a period of 30 minutes and then averaged. The four curves displayed in Figure 4 are for the various polarization combinations, *P*-input and *P*-output polarization, *Mixed*(*S* and *P*)-input and *P*-output, *S*-input and *P*-output, and *Mixed*-input and *S*-output.

To understand what is causing the observed potential dependence in the SH response, the possible contributing factors must be considered. The second harmonic intensity, $I^{2\omega}$, from the interface originates from the nonlinear polarization induced by the fundamental driving field at frequency ω.[17]

$$I^{2\omega} = \left|P^{2\omega}\right|^2 \qquad (1)$$

where the nonlinear polarization, $P^{2\omega}$, giving rise to the SHG is expressed as

$$P^{2\omega} = \varepsilon_o \chi^{(2)} E^2(\omega) \qquad (2)$$

where ε_o is the permitivity of a vacuum, $\chi^{(2)}$ is the surface nonlinear susceptibility tensor and $E^{2(\omega)}$ is the intensity of the driving field at frequency (ω). The elements of the nonlinear susceptibility tensor can be obtained by judicious selection of input and output polarization combinations. In an electrochemical system there is an additional term in the second order nonlinear polarization involving the presence of the static dc field across the interface.[17] The second order nonlinear polarization, $P^{2\omega}$, in the presence of a dc field can be written as

$$P^{2\omega} = \varepsilon_o \chi^{(2)} E^2(\omega) + \varepsilon_o \chi^{(3)} E^2(\omega) E_{dc} \qquad (3)$$

where E_{dc} is the field strength of the dc field and $\chi^{(3)}$ is the third order nonlinear susceptibility tensor. If the third order contribution to the SH response is large the SH response measured for the various polarization combinations will exhibit different potential dependencies due to the directionality of the dc field and that of the $\chi^{(3)}$ elements composing the nonlinear susceptibility tensor.

Referring back to Figure 4, all polarization combinations display the identical potential dependence taking into account the Fresnel factors for the incident and transmitted optical fields. The fact that all the polarization combinations show the same potential dependence suggest that $\chi^{(3)}$ contributions to the SH response are negligible. If the dc field strength was stronger, one would expect a much larger coupling to $\chi^{(3)}$ giving rise to different potential dependencies for the various polarization combinations. This is indeed true for higher electrolyte concentrations where the magnitude of the dc field at the interface is considerably stronger. The results of the concentration dependent studies will be presented in a later publication.

As a result of the negligible contribution from a dc field effect on the SH response, Equation (2) is the most appropriate to use in modeling the observed potential dependence. The observed SH signal potential dependence is attributed to a resonant SH effect. A resonant SH effect occurs when either the fundamental, here at 532nm, or the SH at 266nm are resonant with an optical transition in the material. Returning to the absorption spectra for the neat solvent, 1,2-dichloroethane (12.6 M) and a solution of TBATPB in acetonitrile (0.1mM) shown in Figure 3, there is negligible absorption in the visible region. It is only in the ultraviolet region that appreciable absorption occurs. The spectrum for the 0.1mM TBATPB in acetonitrile shows an absorption at 266nm resulting from a $\pi \rightarrow \pi^*$ transition of the phenyl rings in the TPB^- moiety. The calculated molar absorptivities of DCE and TBATPB at 266nm are 6.2×10^{-3} and 3.3×10^{3} L/mol·cm respectively, as determined from the data in Figure 5. The absolute magnitude of $\chi^{(2)}$ in this case is then related to the molar absorptivity (ε) and the resonant optical frequency (ω_o) in the following way:

$$\chi^{(2)} \propto \frac{N\sqrt{\varepsilon}}{(\omega_o - 2\omega)} \qquad (4)$$

where N is the molecular density or concentration of molecules at the surface and 2ω is the frequency of the SH light. By examination of Equation (2) the observed SH intensity is then dependent upon the square of the surface concentration (N) and directly proportional to the extinction coefficient (ε). Since there a difference in the extinction coefficients of TBATPB vs. DCE of six orders of magnitude. Taking into consideration the concentration of each substance at the interface, there should be at least four orders of magnitude difference between the SH intensity arising from the supporting electrolyte (TBATPB) over that from the bulk solvent (DCE). The fact that the light at 266nm is near resonance with an optical transition of the TPB^- ion results in a further increase in $\chi^{(2)}$ due to the frequency dependent denominator of Equation (4). In this way the detected SH signal can be solely attributed to the TPB^- ion at the interface.

The conclusion that the potential dependent SH response is arising from the TPB^- ion at the interface can also be substantiated by the cyclic voltammogram. By examining the standard Gibbs energies of ion transfer across the water/DCE interface, the ions responsible for current flow in the CV of Figure 5 can be determined. The standard Gibbs energies for transport of an ion from the organic (o) to the aqueous (w) phases are 35.1kJ/mol and 21.8kJ/mol for TPB^- and TBA^+ respectively. The corresponding values for Cl^- and Li^+ are -46.4 kJ/mol and -54.0kJ/mol.[27,28] The value for Li^+ was inferred from data on the water/nitrobenzene interface. From these values, the positive current in the CV (Figure 5) at potentials greater than 400mV is mainly due to the transfer of TPB^-

ion and the negative current at potentials less than 100mV is due to that of TBA^+ from the organic to the aqueous phase. The current due to the transport of Cl^- and Li^+ is considered to be minimal from the comparison of the standard Gibbs energies of ion transport. From this analysis the observed increase in the SH response (Figure 4) at positive potentials correlates with the positive current flow in the CV of Figure 5 which is attributed to the transfer of TPB^-.

The resonance enhanced SH response from the TPB^- ion provides a basis for the relative determination of the TPB^- ion concentration at the interface as a function of the applied potential. The square root of the SH signal intensity, $\sqrt{I_{SHG}}$, is proportional to the concentration of the TPB^- ion at the interface, Eqns. (3) and (4). In this way, the potential dependent SH data can be used to make an optical measurement of the interfacial concentration of the TPB^- ion as a function of the applied potential. To demonstrate this point, the SH signal level obtained at an applied potential of 20mV is found to be comparable to that obtained for the neat H_20/DCE interface. At this potential, the TPB^- ion is drawn away from the interface towards the counter electrode in the organic phase. As a consequence, the concentration of TPB^- at the interface is depleted since the potential drop in the organic phase is due mainly to the TBA^+ ion present in the organic phase space charge region.

TIR SHG provides a powerful means by which to study the electrochemical interface between two immiscible electrolyte solutions. Attempts are being made to correlate the potential dependent SH data with the measured surface excess of tetraphenylborate determined from electrocapillary and capacitance measurements. Since SHG is allowed, under the dipole-approximation, only in regions where material is distributed in an anisotropic manner, the measured SH signal is assumed to be arising from the entire space charge region. The space charge region represents a spatial gradient of electrolytic species responsible for the potential drop across the interface. This gradient in the electrolyte concentration and subsequent solvent density constitutes an anisotropic region extending from the interphase boundary. For this reason attempts are also being made to compare the magnitude of the potential drop across the interface (Galvani potential) and the potential dependent SH data by means of the Gouy-Chapman model.[12] The results of these continuing studies will be presented in a later publication.

Conclusion.

To summarize, the technique of TIR SHG has been applied to the n-alkane/water and water/DCE interfaces. For the water/DCE system, it was shown that the transmitted SH component can be utilized when the reflected SH light is attenuated by the bulk liquid. By employing the transmitted component, the potential dependent SH response for the ITIES composed of an aqueous solution of 1.0 mM LiCl and 1.0 mM TBATPB in DCE was obtained. A minima and maxima in the SH response was found when the aqueous phase is biased negative and positive of the organic phase respectively. The potential dependent SH response is attributed to a resonant enhanced process arising from the potential dependent concentration of the TPB^- ion at the interface. The successful demonstration of the use of TIR SHG at the ITIES greatly expands the capability to study ion adsorption and transport at liquid/liquid interfaces. TIR SHG measurements are a compliment to electrocapillary and capacitance measurements in the determination of electrolyte surface excess. Due to the surface specificity of SHG, the relative concentration of the electrolytic species responsible for the potential drop in the electrochemical double layer may be accessible. Even more fundamental questions may be addressed such those concerning the specific or non-specific adsorption of electrolyte at the ITIES. The use of TIR SHG at liquid/liquid junctions provides a means by which the properties and processes of this broad range of interfaces can be studied.

Figure Captions.

Figure 1. Diagram of the cylindrical quartz cell used for the electrochemical and SHG measurements. The cell contains the aqueous 1.0 mM LiCl and organic 1.0 mM TBATPB solutions (a) and (b) respectively. The Luggin capillaries in the aqueous and organic phases are denoted by (c) and (d). A 1.0 mM aqueous solution of TBACl is used in (d). Additional components of the cell are (e) and (f) the Ag/AgCl reference electrodes and (g) and (h) the platinum counter electrodes. The rays (i) and (j) represent the incident and reflected fundamental at 532nm and (k) the transmitted SH at 266nm. The attenuated reflected SH response is shown by (l).

Figure 2. SH intensity (P_{in} , P_{out} polarization combination) versus incident angle (θ) for (a) decane/water in reflection and (b) water/DCE in transmission. The solid lines in each plot represent the SH response calculated from theory.

Figure 3. UV-Vis absorption spectrum for DCE (———) and 0.1 mM TBATPB in acetonitrile (– – – – –).

Figure 4. Potential dependent SH signal for the 1.0 mM LiCl (H_2O) / 1.0 mM TBATPB (DCE) interface. The following polarization combination are shown (&) P_{in}, P_{out}, (%) $Mixed_{in}$, P_{out}, (Σ) S_{in}, P_{out}, and (E) $Mixed_{in}$, S_{out}.

Figure 5. Cyclic voltammogram for the interface between an aqueous 1.0 mM LiCl and 1.0 mM TBATPB solution in DCE. The current was measured at a scan rate of 5 mV/sec as a function of the potential difference between the aqueous and organic phases, E_w-E_o.

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