Salt Effect on the Formation of Dye Aggregates at Liquid/Liquid Interfaces Studied by Time-Resolved Surface Second Harmonic Generation

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The present study reports on the effect caused by sodium salts added to a solution of malachite green in a liquid/liquid interfacial system probed by the time-resolved surface second harmonic generation (TRSSHG) technique. This effect is known as "salting-out effect" and is shown to reveal two main issues: salts added to the bulk, first, cause a reduction of the dye solubility and, second, stimulate the adsorption of malachite green cations at the interface, changing the equilibrium constant between the dye molecules adsorbed at the interface and those being dissolved in the bulk. The increased adsorption at the interface is observed in the TRSSHG experiment as a relative increase of the aggregates' contribution to the measured time profile. However, depending on the nature and properties of salt anions, the mechanisms responsible for enhancing the population of interfacial aggregates can differ. This study explains such mechanisms for NaCl and NaSCN: addition of NaCl leads to an increase of the malachite green adsorption at the interface followed by the formation of aggregates, whereas the addition of NaSCN leads rather to the formation of aggregates already in the bulk with their further migration toward the interface. A simple quantitative description of the salting-out effect based on a modified Frumkin−Fowler−Guggenheim model also has been proposed. It has been shown to give a good agreement with the experiment with NaCl, i.e., when the formation of dye aggregates in the bulk solution can be neglected.

Introduction

The traditional interpretation of experimental findings obtained by surface tension and surface electric potential measurements has changed over the last two decades as a result of new investigations of the interfacial structure of aqueous electrolyte solutions. Previous experiments, based on a macroscopic approach, have revealed that ions exhibit a monotonically increasing concentration toward the bulk, leaving the outermost liquid layer essentially depleted of ions.[1−3] More recent studies, carried out with surface-sensitive techniques[4−7] such as vibrational sum frequency generation (VSFG) and surface second harmonic generation (SSHG),[8,9] lead to a more complicated picture: small nonpolarizable hard anions are repelled from the aqueous surface in agreement with the traditional picture based on continuum solvent models (i.e., behave "classically"), whereas polarizable soft anions exhibit a nonmonotonic interfacial distribution being enhanced at the outermost surface layer and depleted in the subsurface, where cations, in turn, are enhanced.

As has been shown in a very recent study carried out by measurements of the stationary SSHG intensity, anions adsorbed at the interface attract organic cations by Coulomb interactions and lead to a significantly higher organic dye adsorption at air/liquid interface.[10] The excess negative charge density at the interface increases with the square root of the bulk anions concentration. The leading role of electrostatic forces in the mechanism of enhanced adsorption of an organic dye, malachite green (MG),[11−13] has been confirmed by a very good agreement of the proposed model with the experimental data.

Studies on ions at interfaces frequently involve various thiocyanate salts. Numerous papers by Viswanath et al.[14−16] are devoted to the VSFG investigation of thiocyanates affecting the interfacial water structure and the lipid chain ordering. It has been demonstrated that the concentration of thiocyanate anions at the interface is higher compared to the bulk and, at the same time, the structure of interfacial water is significantly modified.[14]

The thiocyanate anion is classified in the Hofmeister series as a salting-in agent,[17] i.e., its salts enhance the solubility of proteins in aqueous solutions and reduce the number of macromolecules adsorbed at the surrounding aqueous surface.[14−16] On the contrary, addition of NaSCN to aqueous solutions of MG has been found to provoke a huge enhancement of the SSHG efficiency at air/water and alkane/water interfaces revealing a rise of the number of dye molecules adsorbed at an interface. Time-resolved SSHG experiments with MG at the air/water interface carried out by Punzi et al.[18] show that the enhancement of the second harmonic (SH) intensity by addition of NaSCN to the bulk phase is accompanied by a remarkable slow down of the excited state dynamics of MG. It has been proposed that the increase of the SH intensity upon addition of salt is not only due to an enhanced adsorption of the solute molecules at the interface but also due to the formation of MG aggregates.

Combined experimental and theoretical studies on thiocyanide adsorption at the air−water interface[19−23] reveal a simple Langmuir behavior of the SCN^- surface concentration with respect to the bulk, contrary to the adsorption of organic ions, where the interaction between adsorbed ions has to be taken into account when correctly describing the relation between surface and bulk concentrations.[22]

Adsorption of organic ions at different interfaces has been a subject of numerous studies by VSFG as well as by stationary and

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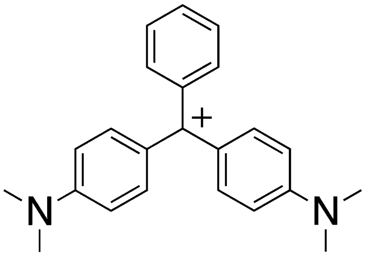

Figure 1. Malachite green cation.

time-resolved second harmonic generation (TRSSHG).[8,9,18,24−33] Investigations of the photoisomerization of MG at air/liquid and liquid/liquid interfaces have evidenced a slower electronic relaxation of the dye at the interface than in the bulk solution. MG (Figure 1) is known to have a very short excited-state lifetime in nonviscous environment as a result of a nonradiative deactivation involving the rotation of all three phenyl and aniline rings and is thus a convenient probe of interface properties.[24,25,28]

The present study, carried out at liquid/liquid interfaces, focuses on the salting-out effect, i.e., the increase of the solute concentration at the surface upon addition of various inorganic sodium salts into aqueous solutions of MG. TRSSHG has been used to monitor the relative concentration of MG aggregates adsorbed at the interface as a function of bulk dye and salt concentrations. The results have been compared to the data reported in several studies on the adsorption of inorganic ions at air/water interfaces.[8,10,18,28] A model proposing a simplified quantitative description of the interaction between the adsorption of inorganic (salts) and organic ions (MG) is also presented.

Experimental Section

Samples. Malachite green oxalate, NaCl, and NaSCN have been purchased from Fluka, whereas Na_2SO_4 and NaBr were from Merck. All compounds have been used without further purification. MG has been dissolved in deionized water to a concentration specified further for each measurement. The following liquids have been used as the upper layer for SSHG samples: *n*-heptane (Acros Organics, 99%+), octane (Aldrich, 98%), decane (Fluka, purum), dodecane (Acros Organics, 99%), tetradecane (Acros Organics, 99%), and pentadecane (Aldrich, 98%). All compounds have been used as supplied. The pH of all samples has been observed between 2.8 and 3, which ensures MG to be present in monocationic form in the investigated solutions. No significant degradation of the samples has been observed after the measurements. The preparation of the samples as well as all the measurements have been done at room temperature.

Setup. The investigated interfacial system was constituted of two immiscible liquids: the upper phase was an *n*-alkane having an index of refraction bigger than that of the lower phase, which was an aqueous solution of MG. A simplified scheme of the TRSSHG setup used in this study is presented in Figure 2.

Femtosecond probe pulses (Ti:Sapphire, 800 nm, 10−100 nJ) were directed at the interface at an angle several degrees larger than the critical angle for total internal reflection. The lower phase of the sample was a solution of MG, which has a $S_2 \leftarrow S_0$ absorption band around 400 nm, the wavelength of the second harmonic signal. Therefore, the presence of MG molecules at the interface increases by orders of magnitude the SHG signal due to a resonance enhancement.[25]

The pump pulses (615 nm, 2 μJ) generated by a noncollinear optical parametric amplifier (NOPA Clark-MXR) were overlapped with the probe pulses at the interface. The wavelength of the pump pulse coincides with the $S_1 \leftarrow S_0$ absorption band of MG. If the excitation pulse precedes the probe pulse, the intensity of the SSHG signal decreases because the molecules in the excited state no longer contribute to the resonant enhancement. The SHG intensity is thus the weakest when the delay between the pulses is small and increases when the delay increases, because more dye molecules have relaxed back to the ground state within the time between pump and probe pulses. The probe and pump pulses were linearly and circularly polarized, respectively. The second harmonic light generated at the interface was collected with a 100 mm focal length lens, filtered from the accompanying scattered fundamental light with a BG23 filter and focused onto the entrance slit of a monochromator (0.25 m Cornerstone from Oriel) equipped with a photomultiplier tube (Hamamatsu, R446). The output signal was amplified and processed by a gated boxcar integrator and averager module (SR250 from Stanford Research Systems) and finally recorded by a computer.

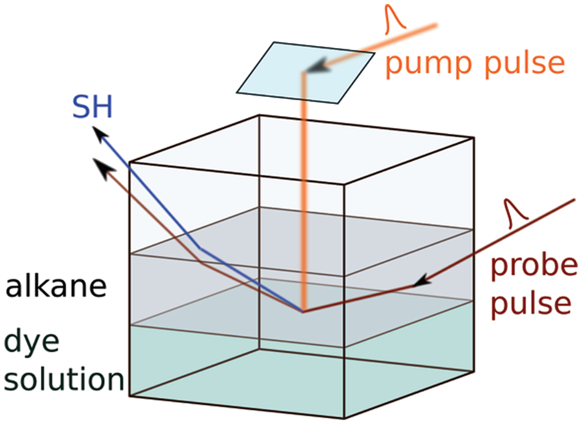

Figure 2. Scheme of the pump−probe TRSSHG experimental setup.

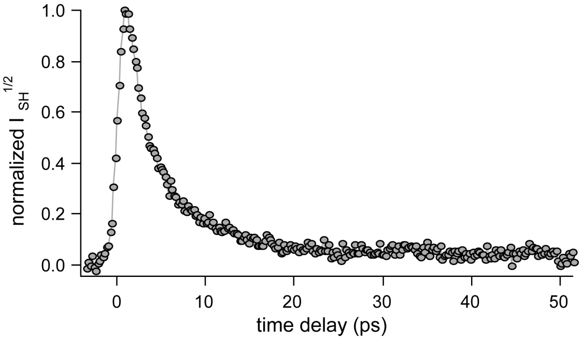

Figure 3. Typical time profile of the processed TRSSHG signal measured with MG at the decane/water interface.

Since the SHG detection is homodyne, the signal intensity is proportional to the square of the contributing population. Thus, the square root of the measured SH intensity is linearly proportional to both the amplitude of the SH electric field and to the number of MG molecules at the interface contributing to the SHG resonant enhancement. Therefore, the SHG signal recorded at the alkane/water interface was put into its final form by taking its square root and by normalization, so that it is 0 for negative time delays and 1 at its maximum. Its typical dependence on the delay between the pump and probe pulses is shown in Figure 3.

Such time profile reflects the ground state recovery dynamics of MG.

It has been shown that the SHG signal decays measured with MG can be both single- and biexponential depending on the

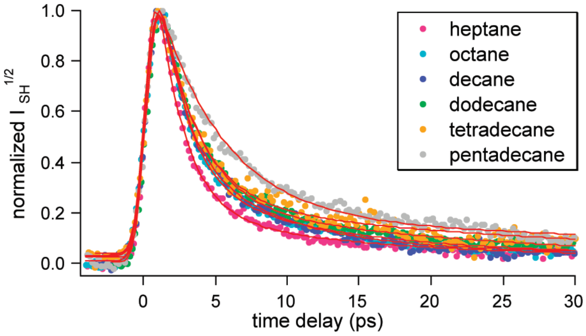

Figure 4. Time profiles of the processed TRSSHG signal measured with MG at different alkane/water interfaces. The red line shows the best fit to the time profiles.

interfacial system.[18] The faster component is attributed to the deactivation of excited monomeric MG molecules, whereas the longer component is attributed to the deactivation of excited aggregates.[18,28] Thus, the recorded SHG kinetics were fitted by the sum of two exponential functions convolved with a Gaussian instrument response function $f(t)$:

$$s(t) = f(t) \otimes (A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + s_0) \qquad (1)$$

where A_1 and A_2 are decay amplitudes corresponding to the deactivation of monomers and aggregates, respectively, and s_0 accounts for a weak long-lived decay component also observed in the data. The origin of this component is unclear but its contribution is so small, less than 10% in most cases, that it will be neglected in further discussion. Thus, when analyzing several time profiles simultaneously, for example, profiles recorded with different salt concentrations, both short and long decay times τ_1 and τ_2 can be kept constant. In this sense, the relative magnitude of A_2 on the salt concentration of the lower phase appears to be of interest, since it indicates the formation of dye aggregates.

Results and Discussions

To comprehend the nature of the processes occurring in the interfacial systems, a number of measurements with different alkanes and salts have first been carried out.

Measurements with Different Alkanes without the Addition of Salt. A first series of measurements has been done with 6 alkanes of different chain length: heptane, octane, decane, dodecane, tetradecane, and pentadecane. The MG concentration in the lower phase has been kept at 1.5 × 10^{-4} M. All the obtained SHG time profiles have been analyzed with eq 1 (Figure 4). The short and long decay times, τ_1 and τ_2, have not been kept constant for this fit, since this particular experiment is not expected to give any information about the aggregate formation, but aims to determine decay times for systems with different alkanes.

The decay times and the corresponding amplitudes obtained from the fit are displayed in Table 1.

From the data in Table 1, one cannot see any clear dependence of the short decay time of MG on the nature of the alkane. At the same time, the average decay time with pentadecane is longer than that with the other alkanes. This effect seems to be specific to pentadecane, and has been observed before.[28] The dependence of the short decay time on the alkane chain length is presented in Figure 5.

TABLE 1: Short and Long Decay Time Constants (τ_1 and τ_2, respectively) and Corresponding Normalized Amplitudes (A_1 and A_2) Obtained with MG at Various Alkane/Water Interfacial Systems

alkane	τ_1, ps	A_1	τ_2, ps	A_2
heptane	1.5 ± 0.1	0.81 ± 0.01	7.1 ± 0.4	0.19 ± 0.01
octane	1.3 ± 0.1	0.82 ± 0.01	6.9 ± 0.3	0.18 ± 0.01
decane	1.5 ± 0.2	0.74 ± 0.04	6.3 ± 0.4	0.26 ± 0.03
dodecane	2.4 ± 0.1	0.83 ± 0.02	15 ± 1	0.17 ± 0.02
tetradecane	1.5 ± 0.2	0.71 ± 0.03	8.1 ± 0.7	0.29 ± 0.02
pentadecane	2.6 ± 0.2	0.63 ± 0.02	11 ± 1	0.37 ± 0.01

This result is in agreement with previous measurements with MG in other air/liquid and liquid/liquid systems.[18,24,28]

Measurements with Octane and Tetradecane upon Addition of Different Sodium Salts. To investigate the effect of salt, a series of measurements with two different alkanes, the more viscous tetradecane and the less viscous octane, have been done. For these experiments, four different salts, NaCl, NaSCN, NaBr, and Na_2SO_4, have been chosen and compared. The concentration of MG has been held at 1.5 × 10^{-4} M. The time profiles recorded at various concentrations of the same salt have been analyzed simultaneously, i.e., all amplitudes A_i in eq 1 have been set free, whereas the decay times τ_1 and τ_2 have been kept constant for the different sets of data. The time profiles obtained with various concentrations of NaCl in the tetradecane/water system as well as the relative amplitudes of the fast and slow decay components with the four salts are shown in Figure 6.

Figure 6 reveals a clear rise of A_2 with the salt concentration. As already mentioned, this amplitude is attributed to the formation of dye aggregates at the interface. Interestingly, the rise of this amplitude seems to saturate with further increase of the salt concentration.

The same analysis has been done for analogous sets of interfacial systems but having octane as the upper layer and qualitatively similar dependencies have been obtained (see Figure S1 in the Supporting Information).

The obtained decay times are presented in Table 2.

All the systems under study exhibit similar behavior: the shorter decay time is equal to approximately 2 ps, whereas the longer one is typically around 10 ps. The amplitude of the slower component increases with increasing salt concentration but the rise seems to saturate at a certain salt concentration. The various salts differ by the concentration at which saturation is reached and the maximum magnitude of A_2.

The difference in the amplitudes behavior when varying alkanes is not very pronounced, allowing some flexibility in choosing alkanes for more detailed investigations of the salt

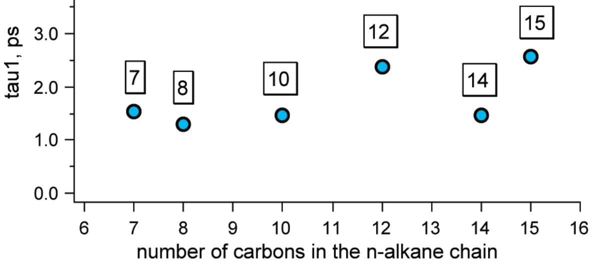

Figure 5. Dependence of the short decay time on the alkane chain length.

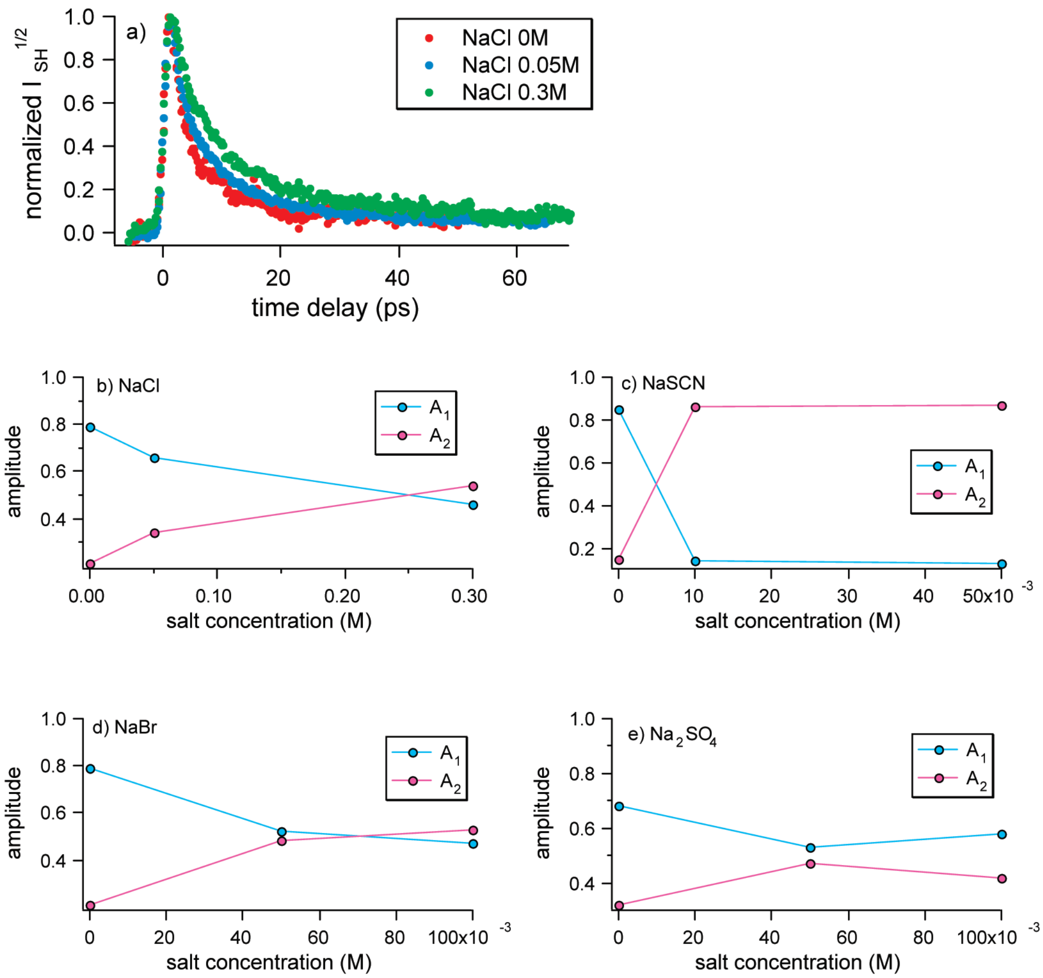

Figure 6. (a) Time profiles of the processed TRSSHG signal measured with MG in tetradecane/water systems without and with addition of NaCl at different concentrations; (b–e) dependences of the amplitudes on the salt concentration with NaCl, NaSCN, NaBr, and Na_2SO_4. The connecting lines in panels b–e are to guide the eyes only.

TABLE 2: Decay Times Obtained from the Biexponential Analysis of the Time Profiles Measured with MG at Interfaces

interfacial system	τ_1	τ_2
octane/water + NaCl	2.2	12
octane/water + NaSCN	2.6	17
octane/water + NaBr	2.4	8.4
octane/water + Na_2SO_4	2.0	9.4
tetradecane/water + NaCl	1.9	11
tetradecane/water + NaSCN	2.5	19
tetradecane/water + NaBr	2.5	12
tetradecane/water + Na_2SO_4	1.7	8.8

effect. However, the observed salt effect depends substantially on the nature of salt anions. From our data, the salt effect increases in the following order: $SO_4^- < Cl^- < Br^- < SCN^-$.

For further studies, only two salts have been selected: NaSCN as the salt that exhibits the strongest effect, i.e., saturation of A_2 is reached at very low salt concentration and A_2 reaches a high value, and NaCl, for which the salt effect is less pronounced.

Measurements with Dodecane upon Addition of Two Different Salts. Detailed studies on the effect of NaSCN and NaCl on the formation of MG aggregates have been carried out at the dodecane/water interface with a MG concentration of 10^{-5} M, i.e., 15 times lower than in the preliminary experiments in order to reduce formation of aggregates in pure water solution. As in the previous data analysis, the simultaneous fit has been employed. Since the two associated time constants are attributed to monomeric and aggregated forms of the same dye, their values should not depend on a particular salt added to the bulk solution. Therefore, all time profiles recorded with both NaSCN and NaCl have been analyzed simultaneously and the time constants have been kept equal for all decays. The dependences of the decay amplitudes A_1 and A_2 on the salt concentration are shown in Figure 7. The short and long decay time constants have been found to be $\tau_1 = 2.1$ and 13 ps. These values and the dependence of the amplitudes on the salt concentration are very similar to those observed in the preliminary measurements at higher MG concentration.

The results at liquid/liquid interfaces can be compared with those obtained with the air/liquid system studied previously:[18] in those experiments, the influence of the addition of salts on the stationary SH intensity as well as TRSSHG profiles have been investigated. The SH intensity has been found to rise with increasing salt concentration and to saturate at high concentrations. This resembles the behavior of the decay amplitude A_2 (in Figure 7), which reflects the formation of MG aggregates at the interface. The dependence obtained in ref 18 has been interpreted as follows: the increase of the SH intensity upon addition of salt is not only due to an enhanced adsorption of the MG molecules at the air/liquid interface but also due to the formation of aggregates. Comparing the results at air/liquid and liquid/liquid interfaces, one can conclude that the increase of salt concentration enhances MG aggregation at both types of

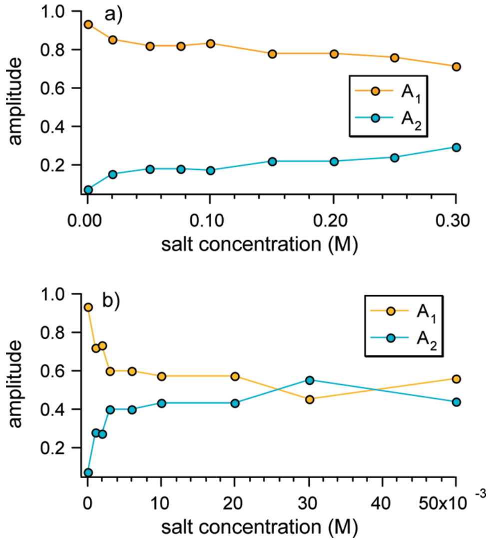

Figure 7. Dependences of decay amplitudes on the salt concentration measured with MG at a dodecane/water interface:(a) NaCl and (b) NaSCN. The connecting lines are guides to the eyes only.

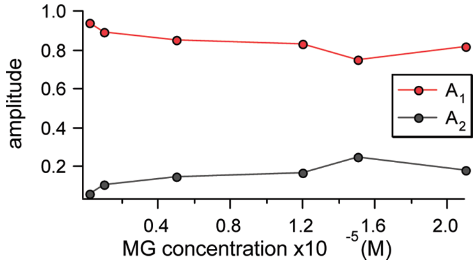

Figure 8. Dependence of decay amplitude components on MG concentration measured at the dodecane/water interface. The connecting lines are guides to the eyes only.

interfaces and, hence, the SH intensity. The so-called salting-out effect takes place: the presence of salt anions leads to an increase of the number of MG molecules at the surface and, hence, increases the probability of the aggregate formation.

The gain of the amplitude A_2 with increasing salt concentration can be compared to the increase of A_2 with increasing dye concentration. Such dependence is presented in Figure 8: it can be seen that in this case as well, the contribution of the decay component attributed to the deactivation of aggregates increases with the bulk concentration of the dye and that finally a saturation is reached. The saturation value of A_2 is, however, much lower in pure water solution than in the system containing salts.

One can conclude that showing the gain of A_2 with the bulk concentration, both graphs, in fact, reflect the increasing number of MG molecules at the interface: in the first case (Figure 7), it is provoked by the rising number of salt anions in the bulk, whereas in the second case (Figure 8) it is done by the rise of the dye concentration. This once again demonstrates that the addition of anions stimulates to a different extent the migration of MG cations toward the interface favoring thus aggregation. The difference observed between NaCl and NaSCN reflects the effect of the salt anion.

At least two aggregation mechanisms are possible: the addition of salt increases the amount of MG cations being adsorbed at the interface and MG aggregation occurs directly at the interface; or, MG aggregation occurs already in the bulk and then the migration of these aggregates toward the interface takes place. To find out which of these mechanisms prevails, the absorption spectra of MG without and with the addition of salts (NaCl and NaSCN) have been measured (Figure 9).

From Figure 9, one can see that the absorption spectrum of MG does not change much when varying NaCl concentrations (Figure 9a), whereas it changes remarkably upon addition of NaSCN (Figure 9c). Comparing normalized spectra of MG with NaCl (Figure 9b) and NaSCN (Figure 9d), one can see that addition of NaSCN leads to increasing absorption on both sides of the $S_1 \leftarrow S_0$ absorption band of MG. These features can be attributed to the aggregation of MG;[18] moreover we can conclude that the aggregates are formed by MG cations, because the spectral changes accompanying aggregation are relatively small. If the aggregates were created by the neutral (carbinol) form of MG, the spectral changes would be much more pronounced because the carbinol form does not absorb in the visible range.[8] The effect of the addition of thiocyanide anions to organic dye solutions has already been reported by Barnes[34] and Punzi et al.:[18] both have proposed strong aggregation and precipitation of the dyes upon addition of NaSCN. With NaCl this effect is much weaker as the MG spectra do not demonstrate any significant changes when varying the salt concentration up to 0.3 M. At the moment there is no complete theory of ion−solute interactions, which could explain why NaSCN stimulates MG aggregation so efficiently compared to NaCl. Thiocyanates increase solubility of proteins in water solutions and are known to be salting-in agents in clear opposition to their behavior observed in our experiments. Some works indicate that specific dispersion interactions should be included in the theory in order to explain the salting-in effect of thiocyanates on proteins.[35] Moreover, the high propensity of SCN^- anions to protein/water interface should be responsible for the increasing solubility of proteins upon addition of thiocyanates.[36] It has been proposed that this effect is related to the weak hydration of this anion as measured by neutron diffraction.[37] The weaker free energy of hydration of SCN^- compared to Cl^- could explain the higher concentration of SCN^- at the interface. Furthermore, because SCN^- is poorly hydrated, anions present in the bulk solution may interact with the MG cations and reduce their solubility and hence enhance the aggregation of MG. Consequently, the following hypothesis about the influence of salts on aggregation can be proposed: addition of NaCl does not lead to significant aggregation in the bulk, but instead increases the number of MG cations adsorbed at the interface, so that the formation of MG aggregates occurs mainly at the interface. On the other hand, addition of NaSCN increases the amount of aggregates being formed already in the bulk with a further migration toward the interface.

The same conclusion about the aggregation mechanism also can be drawn when trying to find a proper fit to the measured decay amplitude A_2. The authors of ref 22 suggest the Frumkin−Fowler−Guggenheim (FFG) model to reproduce the dependence of the concentration of interfacial molecules on the bulk concentration. This model is a variant of the Langmuir model, which, in turn, assumes the partition of the system into bulk and surface regions and postulates a chemical equilibrium for the exchange of solvent and solute molecules between two regions. Extending the Langmuir model, the FFG model accounts for the interaction between the solute molecules at the surface. This model results in the following relationship between the bulk concentration C and the fractional surface coverage $\theta = N_s/N_s^{max}$, where N_s is the number of solute molecules at the interface and N_s^{max} the maximum possible number of molecules at the surface:

$$\frac{\theta}{1-\theta}\exp(-g\theta) = K'C \qquad (2)$$

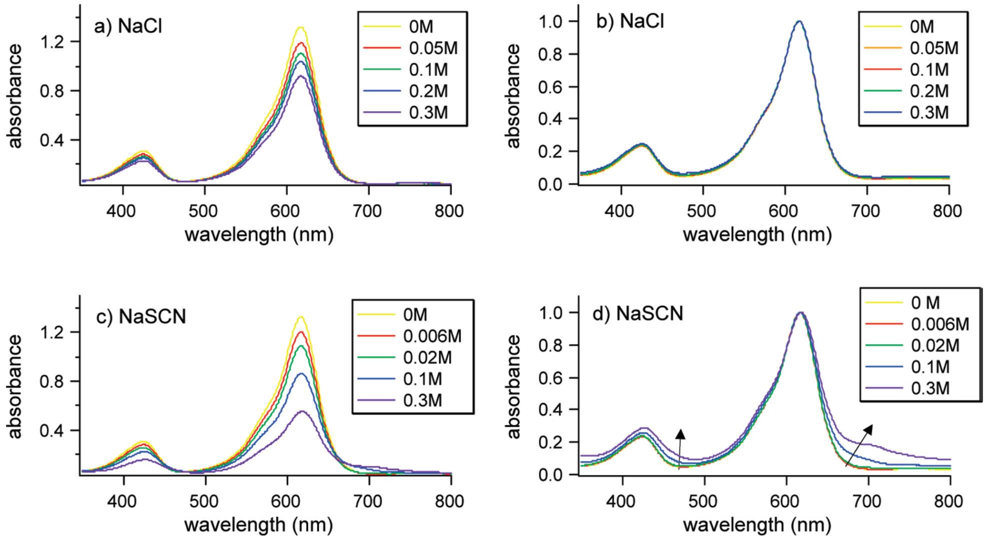

Figure 9. Absorption spectra of MG at 10^{-5} M in water with various concentrations of salts: (a and b) measured and normalized spectra with NaCl, respectively, and (c and d) measured and normalized spectra with NaSCN, respectively. The arrows illustrate the spectral broadening.

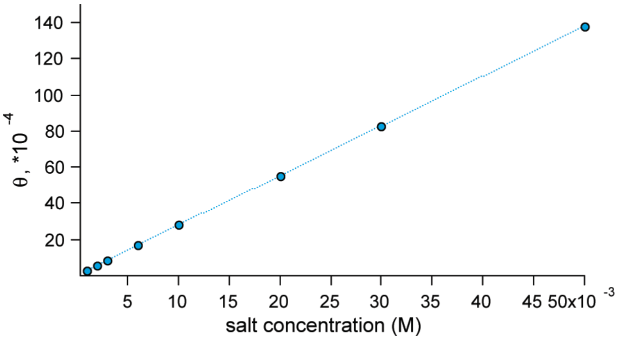

Figure 10. Dependence of the fractional surface coverage of SCN^- at an air/water interface on the bulk salt concentration calculated from eq 4.

where g is an interaction parameter, eq 2, with $g = 0$ yielding the Langmuir model, and K' is a modified equilibrium constant, a modified Langmuir constant. This model has been used to describe the adsorption of organic ions, such as tetrabutylammonium iodide, at air/liquid interfaces and has given a significantly better agreement with the experimental data than the Langmuir model.[22] On the other hand, for small inorganic ions, the Langmuir model has been shown to give a satisfactory agreement with the experiment.[23] In the latter case, the fractional coverage of ions at the surface of a water solution can be expressed as

$$\theta = \frac{C}{C + 55.5M\exp\left(\frac{\Delta G_{ads}}{RT}\right)} \tag{3}$$

where ΔG_{ads} is the Gibbs free energy of solute adsorption to the interface, and RT is the product of the gas constant and temperature. The free energy of adsorption of SCN^- at the air/water interface has been found to be $\Delta G_{ads} = (-6.7 \pm 1.1)$ kJ/mol.[23] With this value, the dependence of the surface concentration of the ions on the bulk salt concentration, which has been shown to increase with a square root of the bulk concentration of anions,[10] is practically linear at low concentrations (Figure 10). Although this result has been obtained for air/water interface and for SCN^- only, it is safe to assume that at the low salt concentrations used in the present study, this linear dependence remains valid for liquid/liquid interfaces as well as for Cl^-.

Further, we assume that the presence of salt anions at the interface increases the equilibrium constant K' for the adsorption of the dye and that this increase is proportional to the surface concentration of the anions. Therefore, K' in a system where the salt concentration is equal to C_{salt} can be expressed as

$$K'(C_{salt}) = K'_0 + \kappa\cdot C_{salt} \tag{4}$$

where K'_0 is the equilibrium constant for dye adsorption in pure water solution and κ is a proportionality coefficient.

Assuming a linear relation between θ and A_2, $\theta = \alpha\cdot A_2$, and substituting K' in eqs 2 by eq 4, one can obtain a relationship between the slow decay amplitude and the bulk salt concentration:

$$\frac{\alpha A_2}{1 - \alpha A_2}\exp(-g\alpha A_2) = (K'_0 + \kappa C_{salt})\cdot C \tag{5}$$

Since it is impossible to find an algebraic solution of eq 6 for A_2, the fit has been performed with the inverted dependence $C_{salt}(A_2)$:

$$C_{salt}(A_2) = \frac{1}{\kappa}\left[\frac{\alpha A_2}{C(1 - \alpha A_2)}\exp(-g\alpha A_2) - K'_0\right] \tag{6}$$

The best-fit curve with NaCl obtained with $K'_0 = 0.18$ L/mol and $\kappa = 8$ L^2/mol^2 is presented in Figure 11. Equation 6 fits the data very well, indicating that the simple linear relations between K' and C_{salt}, and also between θ and A_2, assumed when deriving this equation, are a sufficiently good approximation. Figure 11 points to a possible saturation at larger NaCl concentrations. This is expected, since the increase of salt concentration provokes a continuous attraction of MG cations to the interface, which should finally lead to the occupation of all the interfacial sites.

It has to be noted that the FFG model presumes the formation of aggregates at the interface only and does not take into account the mechanism of the bulk aggregation, which, as has been discussed earlier, is most probably provoked by NaSCN

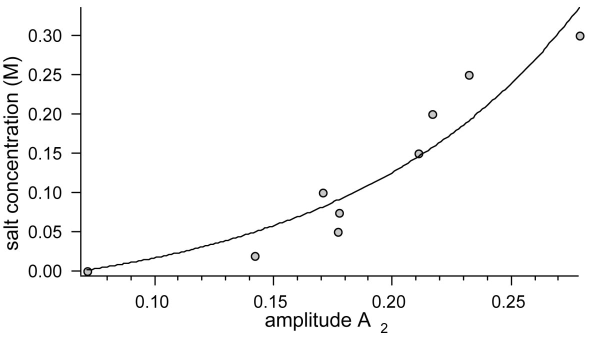

Figure 11. Best fit of the modified FFG model (eq 6) to the experimental data obtained with NaCl.

addition. Therefore, eq 6 is not expected to fit the data measured with NaSCN, and, indeed, it turns out to be impossible to obtain an acceptable agreement of this model with the NaSCN data.

The above analysis interpreted in terms of the results obtained with thiocyanate anions at air/water interfaces[19−23] leads to the following description of the salting-out phenomenon. The primary effect upon addition of sodium salt to a solution of a dye such as MG is the dissociation of salt and the migration of the anions toward the surface. The presence of these anions at the interface shifts the equilibrium between bulk and surface populations of dye cations in favor of the latter and the number of adsorbed dye molecules increases, tending to maintain a chemical equilibrium for the new conditions. The increase of the surface dye concentration leads to aggregation observed as an increase of the SH intensity and a slowing down of the excited-state deactivation of MG in the TRSSHG experiments. This picture, valid for salts exhibiting moderate salting-out effect, changes for thiocyanate salts which have much more dramatic influence on the aggregation at interfaces. Addition of SCN^- to MG solution leads to efficient aggregate formation in the bulk due to a significant reduction of solubility. The positively charged aggregates are attracted toward the surface in a similar manner as monomeric cations and migrate to the interface causing a fast saturation of adsorption.

Conclusions

The present study was aimed to explore and understand processes taking place in interfacial systems, in particular to investigate the salting-out effect observed in TRSSHG experiments as an increase of SH intensity and a slowing down of the excited-state relaxation of MG adsorbed at the interface upon addition of sodium salts. The effect caused by various anions (Cl^-, SCN^-, Br^-, SO_4^-) has been compared, and two of them (Cl^-, SCN^-) have been subjected to a detailed investigation. The study has been carried out at water/alkane interfaces with a series of *n*-alkanes of varying viscosities (from heptane to pentadecane). It has been found that for both cases, i.e., without and with the presence of salts in the lower bulk phase, the variation of alkanes as upper phases does certainly not affect the electronic relaxation of MG excited state.

The effect of salt addition by itself appears as a rise of the slower decay component of the TRSSHG signal. As this component has been ascribed to relaxation of dye aggregates, its increasing contribution to the decay reflects the increasing number of interfacial aggregates. To describe quantitatively the relation between the bulk salt concentration and the amplitude of the slow decay component, a simple modification of the Frumkin−Fowler−Guggenheim model has been proposed. It has been assumed that the adsorption of salt anions at the interface leads to a shift of the equilibrium constant between interfacial and bulk MG in favor of the interface. The increase of the MG adsorption to the interface is followed by the formation of aggregates. Thus, the effect of salt addition has been attributed to the linear increase of the equilibrium constant between surface and bulk dye populations with the concentration of salt. The resulting relationship between the amplitude of the slow decay component and the dye and salt concentrations in a composite system has been satisfactorily fitted to the data obtained with NaCl. A slightly different picture has been suggested to explain the dramatic effect caused by NaSCN. In this case, the addition of salt results in a strong reduction of dye solubility and in the formation of aggregates in the bulk solution already. The aggregates migrating toward the interface occupy the majority of the available adsorption sites and their excited state dynamics predominates the observed time dependence of the TRSSHG signal.

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Supporting Information Available: Dependences of the TRSSHG amplitudes on the salt concentration obtained with NaCl, NaSCN, NaBr, Na_2SO_4, with MG in octane/water systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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