Proton Transfer between Organic Acids and Bases at the Acoustic Bubble−Aqueous Solution Interface

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The multibubble sonoluminescence (MBSL) emission intensity from aqueous solutions containing simple aliphatic organic acids (RCOOH) and bases (RNH$_2$) and mixtures of the two types of solutes has been examined as a function of pH. In solutions containing either an organic acid or base, under pH conditions where the solutes are predominately in their ionized form (i.e., RCOO$^-$ and RNH$_3^+$), the MBSL intensity is identical with that obtained in pure water. Alternatively, under pH conditions where the solutes are in their un-ionized form the MBSL intensity is suppressed. However, in solute mixtures of RCOO$^-$ and RNH$_3^+$ in the pH range of 7 to 9, the MBSL intensity was significantly suppressed relative to that from water. To explain the results of the mixed solute system it has been postulated that when the bubble/solution interface experiences the extreme temperature conditions that accompany bubble collapse, proton transfer occurs between acid−base ion-pair complexes, [RCOO$^-\cdots$RNH$_3^+$], adsorbed at the bubble/solution interface. The neutral forms of the solutes then evaporate into the bubble during its expansion phase and through a complex series of events, over a number of bubble oscillations, reduce the core temperature of the collapsing bubble and hence the SL intensity.

Introduction

Sonoluminescence (SL) is a broad wavelength emission that occurs when a liquid medium is exposed to power ultrasound. The emission occurs at the final stages of the collapse of microbubbles that are generated in sonicated solutions. It is generally accepted that a combination of the electronic relaxation of a plasma and emissions from excited molecular and atomic species are responsible for the broad wavelength spectrum of SL.[1−5]

We have previously reported that surface active solutes may enhance, quench, or have no influence on the SL intensity generated in aqueous solutions, depending on the physicochemical properties of the solute.[6−10] We have also demonstrated that the volatility of surface active solutes is crucial for sonoluminescence quenching in both single and multibubble systems.[6−10] In addition, the degree of SL quenching has been directly correlated with the Gibbs surface excess, i.e., the bubble/solution interfacial concentration, of the volatile surface active solutes in aqueous solutions.[6−10]

Our earlier reports[7,10] on the effect of solution pH on MBSL intensity in aqueous solutions containing aliphatic weak acids such as *n*-propanoic, *n*-butanoic, and *n*-pentanoic acids revealed that the SL was suppressed when the pH of the medium was less than the pK_a of these acids. Similarly, aliphatic weak bases such as *n*-propyl-, *n*-butyl-, and *n*-pentylamines suppressed the SL when the pH of the medium was greater than the pK_a of these amines. That is, under pH conditions where these solutes remained in their neutral forms and hence volatile, the SL was reduced relative to that from water. The actual mechanism responsible for the SL quenching is quite complex. It has been proposed[7,10−12] that volatile solutes drawn into the bubble are thermally decomposed, and hydrophobic products, such as methane, ethylene, etc., accumulate in the bubble over many oscillation cycles, possibly as many as 5000 cycles at 500 kHz

ultrasound.[13] The presence of the products in the bubble in addition to the decomposition reactions in the bubble core contribute to the lowering of the bubble temperature hence the decrease in the SL intensity.

The high sensitivity of the SL intensity in aqueous solutions to the presence of volatile solutes has been used in the present study to investigate the interaction between weak organic acid/base solutes at the acoustic bubble/solution interface.

Experimental Details

The ultrasound source used in all experiments was an in-house modified Undatim Ultrasonics D-Reactor operating at 515 kHz. The reactor was placed in a light-shielded housing which also contained an end-on photomultiplier (Hamamatsu) for detecting the sonoluminescence from the solutions insonated. The emission signals were recorded on a LeCroy 7242 digital oscilloscope, then downloaded onto a Macintosh computer for further analysis. All the work reported here was carried out using 4 ms pulses with 12 ms between pulses. The SL intensity from 100 pulses was averaged. The first 20 pulses were not used in the averaging, as SL produced in these initial pulses had not yet reached a steady-state intensity.[6]

All aliphatic amines and acids used were AR grade and were used as received. Research grade sodium pentylsulfonate was from Sigma. The "Milli-Q" water used to make all solutions had a conductivity of <1 × 10^{-6} S cm^{-1} and a surface tension of 73.8 mN m^{-1} at 18 °C. The pH of the solutions was adjusted with appropriate amounts of HClO$_4$ or NaOH solution. Experiments were conducted at room temperature and any heating of the solutions during sonication was limited to a few degrees. The sonicator was operated at about 15 W. The volume of the solutions sonicated was 25 mL. Surface tension measurements were made using a McVan Analite Surface Tension Meter with a glass Wilhelmy plate.
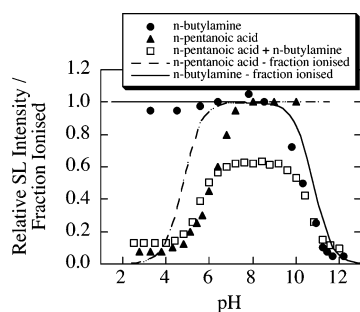
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Figure 1. Relative sonoluminescence intensity as a function of pH observed from air-saturated 0.1 M NaClO$_4$ aqueous solutions containing 25 mM *n*-butylamine, 25 mM *n*-pentanoic acid, and a mixture containing 25 mM *n*-butylamine and 25 mM *n*-pentanoic acid. The solid and broken lines indicate calculated[14] relative concentrations of the ionic forms (RNH$_3^+$ and RCOO$^-$) of *n*-butylamine and *n*-pentanoic acid, respectively.

Results and Discussion

The influence of the solution pH on the sonoluminescence intensity observed from 3 different systems, viz., 25 mM *n*-pentanoic acid, 25 mM *n*-butylamine, and a mixture of 25 mM of each of these solutes in aqueous 0.1 M NaClO$_4$ solutions is shown in Figure 1. The effects observed in the individual solute solutions have been discussed in detail previously.[7] Considering that the pK_a values of these two solutes (*n*-pentanoic acid and butylamine) are ~4.8 and ~10.8, respectively, both these solutes would exist predominantly (>90%) in their ionized, nonvolatile forms (RCOO$^-$ and RNH$_3^+$) above pH ~6 and below pH ~9, respectively.[14] It can be seen in this figure that substantial quenching of the SL intensity only occurs when the individual solutes are in their un-ionized form.

On the basis of the results of the individual solutes and the information above, the SL intensity is not expected to decrease, relative to pure water in the pH range 7−9, as both solutes are present in solution in their ionized, and hence nonvolatile form. However, the experimental results observed show a clear 40% decrease in the SL intensity in the pH range 7−9. As already mentioned it has been well established that the SL generated at 500 kHz is quenched by volatile organic solutes.[6−8,10] Therefore, the suppression of the SL seen may be attributed to organic molecules entering the bubble.

Two possible mechanisms that can be suggested for how this could occur; both involve the formation of a neutral ion pair complex between the alkylammonium and carboxylate species at the bubble solution interface, as shown by reaction 1. Formation of such ion pair complexes has been reported in the literature.[15]

$$RCOO^- + RNH_3^+ \rightarrow [RCOO^- \text{--}^+HRNH_2]_s^{\#} \qquad (1)$$

It would also have to be postulated that the ion pair complex is sufficiently volatile to be able to enter the bubble during its expansion phase, as does a neutral amine or carboxylic acid.[6−10] Although we do not know the volatility of such complexes it can be expected to be very low, considering the ionic nature of the complex. Furthermore, similar net neutral charged species such as alanine[7] at pH values of 6 to 9 and a zwitterionic surfactant[6] show no effect on suppressing SL in aqueous solutions. In addition, in experiments conducted with the cationic surfactant, dodecyltrimethylammonium chloride, and butyric acid under pH conditions where ion-pairing would be excepted no sonoluminescence quenching was observed. Therefore it would have to be considered highly unlikely that the complex enters the bubble to suppress the SL.
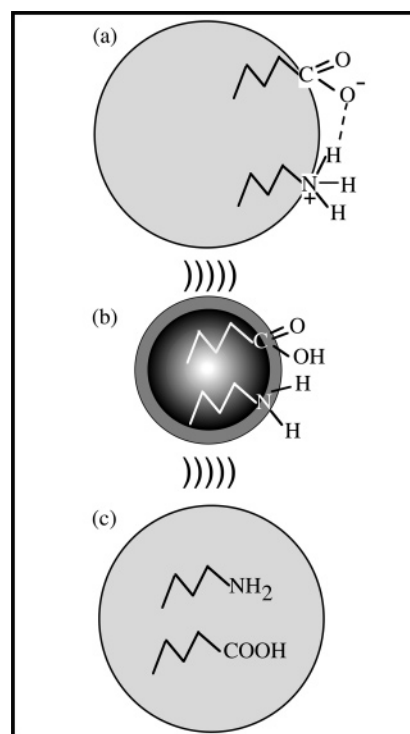

Figure 2. Diagrammatic representation of the proton-transfer reaction at the bubble/solution interface. (a) Ionized forms of the alkyl acid and amine adsorbed at the bubble/solution interface as an ion pair complex due to electrostatic interaction between the charged head-groups. (b) A hot liquid shell surrounding the bubble, formed at the final stages of the collapse, assists proton transfer between the alkylammonium cation and the alkyl carboxylate anion. This leads to the formation of the neutral species at the bubble/solution interface. (c) The neutral solutes evaporate into the bubble in the subsequent expansion phase of the bubble.

The second mechanism that can be proposed involves proton transfer between the organic ions in the ion pair complex at the bubble/solution interface, resulting in the formation of *n*-pentanoic acid and *n*-butylamine in their neutral, volatile, forms (reaction 2).

$$[RCOO^- \text{--}^+HRNH_2]_s^{\#} \rightarrow RCOOH + RNH_2 \qquad (2)$$
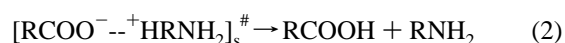
The stimulus for this reaction can be conceived as a consequence of the bubble/solution interface experiencing some of the extreme temperature conditions reached within the bubble during bubble collapse.[16] It has been inferred from rate of reaction experiments that the temperature of the liquid shell (~200 nm thick) surrounding the collapsing bubble can reach close to 2000 K.[16] These high-temperature conditions may be responsible for proton transfer to occur between the ionic solutes that results in the formation of the solutes in their individual neutral forms. As shown schematically in Figure 2, the neutral species formed at the final stages of the collapse can then evaporate into the bubble during the subsequent expansion phase of the bubble and suppress the SL, as observed with any surface active volatile solutes.[6−10] It is also a requirement that back transfer of the proton is slow compared to the expansion time, approximately 1 μs at 500 kHz, over which the interface relaxes back to bulk solution temperatures.

The reason that a high interfacial temperature may provide the conditions for reaction 2 to take place rests with the likely changes in the physicochemical properties of the interface. At this higher temperature, the dielectric constant of the solvent around the bubble can be expected to be much lower than that
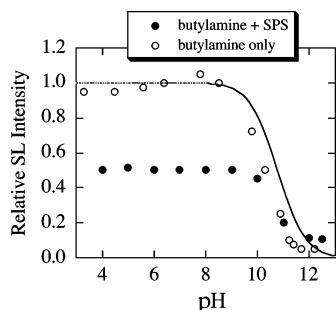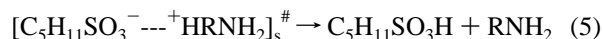
Figure 3. Relative sonoluminescence intensity as a function of pH observed from air-saturated 0.1 M NaClO$_4$ aqueous solutions containing 25 mM *n*-butylamine and 25 mM *n*-butylamine + 25 mM sodium pentyl sulfonate. The solid line indicates the calculated[14] relative concentrations of *n*-butylamine in its ionized form.

of the bulk solution, e.g., the dielectric constant of water at its supercritical point is about 2.[17] This low dielectric constant of the solvent at the interfacial region does not favor the existence of ionic species, and therefore provides the thermodynamic driving force for proton transfer between the ionic solutes within the ion-pair complex, resulting in the formation of neutral forms of these solutes. The second possible explanation for the proton transfer to occur at the interface experiencing the higher temperature is that there may be a shift in the pK_a values of the solutes. In general, with increasing temperature, the pK_a of a carboxylic acid will shift to a higher pH and the pK_a of the alkylammonium ion will shift to a lower pH. However, the latter possibility can be ruled out by the fact that the solutions containing the individual solutes do not show SL quenching in the pH range 7−9.

To support this argument that proton transfer occurs between the acid−base solutes adsorbed at the bubble/solution interface, further experiments were performed with a different mixed system, viz., 25 mM sodium pentylsulfonate (SPS) and 25 mM *n*-butylamine. SPS is a surfactant and strong electrolyte and remains ionized in aqueous solutions (reaction 3) over the pH range studied. The conjugate acid of the alkylsulfonate anion, RSO$_3$H, is a strong acid with a pK_a of less than 2 and remains in the dissociated form in the pH range of 2−13. The pentylsulfonate anion is also adsorbed at the bubble/solution interface due to the hydrophobic character of the hydrocarbon chain. In a mixed solution of SPS and *n*-butylamine, an ion pair complex formation may occur as shown in reaction 4 when the pH is less than the pK_a of the amine.

$$C_5H_{11}SO_3Na \rightarrow C_5H_{11}SO_3{}^- + Na^+ \qquad (3)$$

$$C_5H_{11}SO_3{}^- + RNH_3{}^+ \rightarrow [C_5H_{11}SO_3{}^- \text{---} {}^+HRNH_2]_s{}^\# \quad (4)$$

$$[C_5H_{11}SO_3{}^- \text{---} {}^+HRNH_2]_s{}^\# \rightarrow C_5H_{11}SO_3H + RNH_2 \quad (5)$$

Comparing reaction 1, the carboxylate ion has been replaced by the SPS anion in reaction 4. As in reaction 2, proton transfer between the solutes in this complex would lead to the formation of the neutral species (reaction 5). If reactions 4 and 5 occur, one would expect SL quenching at a pH value less than the pK_a value of the amine. Indeed the SL experiments conducted with these mixed solutes confirmed our prediction. The data in Figure 3 show that the SL is quenched over the whole pH range studied. However, in the pH range below the pK_a of the amine, SL quenching is only about half the amount compared to that in the pH range above the pK_a.

TABLE 1: Surface Tension Measured at $T = 18.2°$C and pH $\sim$8 for the Aqueous Solutions of the Solutes Examined

	surface tension (γ),[a] mN/m
solute	pH 8 **(pH 12)**
water	73.8
25 mM *n*-propylamine	73.4
25 mM *n*-butylamine	72.5 **(68.8)**
25 mM *n*-pentylamine	71.1
25 mM *n*-butanoic acid	73.3
25mM *n*-pentanoic acid	69.9
25 mM *n*-butylamine + 25 mM *n*-pentanoic acid	69.8

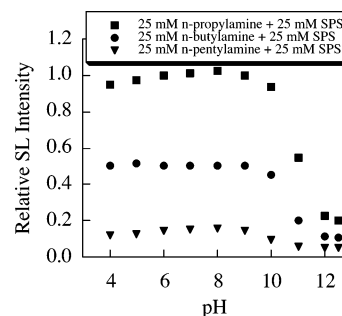[a] Errors estimated to be ±0.1 mN/m.

Figure 4. Relative sonoluminescence intensities at various pH values for the three systems SPS/*n*-propylamine, SPS/*n*-butylamine, and SPS/*n*-pentylamine.

This can be explained by considering the surface activity of the amine as a function of pH. Unlike the surfactant, the interfacial adsorption characteristics of the amine change with the solution pH. For a given concentration of *n*-butylamine, at pH < pK_a the adsorption is lower than that at pH > pK_a. This means that at pH <$\sim$11, the amount adsorbed at the bubble/ solution interface will be lower than that at pH >11. The surface tension data shown in Table 1 support this argument. The surface tension of 25 mM *n*-butylamine solution is 72.5 mN/m when the solution pH is about 8, whereas the surface tension decreases to 68.8 mN/m when the pH is increased to about 12. This leads to a relatively lower surface concentration of RNH$_2$ at the interface formed by reactions 4 and 5, when the solution pH is less than the pK_a of *n*-butylamine. This then leads to a lower SL quenching when the solution pH is less than about 11, as observed in Figure 3.

To support the argument that the presence of solutes at the interface leads to the proton-transfer reactions, further experiments were carried out with the mixed systems: SPS/*n*-propylamine, SPS/*n*-butylamine, and SPS/*n*-pentylamine. In all three systems, the concentration of SPS anion at the interface is constant at all pH values. However, under the condition pH < pK_a, the interfacial concentration of RNH$_3{}^+$ ions increases in the order pentyl > butyl > propyl as indicated by the decrease in the surface tension with an increase in the alkyl chain length of the amine (Table 1). This means that the amount of neutral species formed by proton-transfer reactions will be on the order pentyl > butyl > propyl, which will result in SL quenching on the order SPS/*n*-pentylamine > SPS/*n*-butylamine > SPS/*n*-propylamine. The SL quenching results shown in Figure 4 agree with this expectation and support the earlier argument that the (bubble/solution) interfacial concentration of the ionic forms of the solutes is crucial for the proton transfer to occur.

The above discussion is also supported by further experiments, in which SL from an aqueous solution of 25 mM *n*-alkylamines at a pH of 8 with varying concentrations of SPS was monitored and the results are shown in Figure 5a. At this
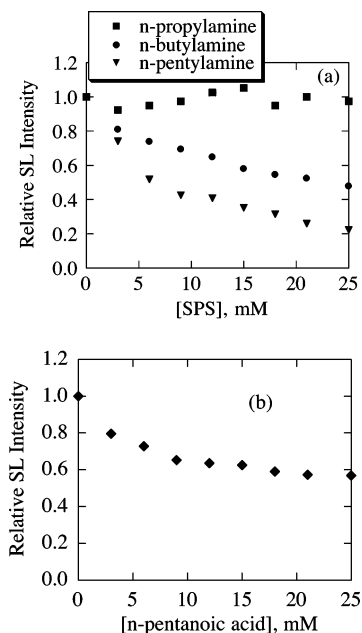
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Figure 5. (a) Relative sonoluminescence intensity observed from air-saturated aqueous solutions containing 25 mM *n*-alkylamines with varying sodium pentyl sulfonate concentrations at a pH of ∼8. (b) The effect of [*n*-pentanoic acid] on the SL intensity observed from 25 mM *n*-butylamine at a pH of ∼8.

pH, *n*-alkylamines will be predominantly in their protonated forms, where no SL quenching occurs. As the concentration of SPS is increased, proton transfer from the RNH_3^+ to pentylsulfonate ion leads to the formation of neutral species as shown in reactions 1−5 leading to an increase in SL quenching. The amount of SL quenching depends on the surface concentrations of the alkylammonium ions as explained earlier. Figure 5b shows that the addition of *n*-pentanoic acid instead of SPS has the same effect.

One final point, although we have suggested that an ion pair complex is the unit involved in the proton transfer, it is not possible to exclude that transfer may also occur between a noncomplexed proton donor and a proton acceptor. However, with a positively and negative charged species adsorbed at the interface it is unlikely they will not be electrostatically bound together and therefore the ion pair complex is the more likely unit involved in the proton-transfer reaction.

Conclusions

The MBSL quenching experiments carried out in aqueous solutions suggest that proton transfer occurs between acid−base ionic solutes adsorbed, probably as an ion pair complex, at the bubble/solution interface. The formation of a hot liquid shell surrounding the collapsing bubble has been proposed as providing the conditions needed for this proton transfer to occur. It has also been shown that the surface concentration of the ionic solutes is important for this proton transfer to occur.

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