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Effect of NaCl salt on sonochemistry and sonoluminescence in aqueous solutions

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Abstract

The presence of salts in a solution is known to affect sonochemistry, but until now no consensus has been reached in the literature on how and why a salt influences sonochemistry. The present study focuses on the effect of NaCl on sonochemical activity and sonoluminescence at 362-kHz frequency in aqueous solutions saturated with He and Ar. It is shown that the presence of salt has a multiple impact: the global population of active bubbles decreases due to the decreasing gas solubility, new chemical reactions involving $Na^{\cdot}$ and $Cl^{\cdot}$ atoms occur that influence hydrogen and hydrogen peroxide yields and the standing wave component of the US wave is enhanced, favoring sonoluminescence emission. Interestingly, the effect of salt greatly depends on the nature of the saturating gas: for instance, strong acidification occurs under He, while it is limited under Ar.

Keywords: sonochemistry, sonoluminescence, salt, NaCl, active bubble population

1. Introduction

During the passage of ultrasound in a solution, chemical activity takes place, referred to as sonochemistry that is due to acoustic cavitation, the nucleation, growth and violent collapse of microbubbles in the solution. The sonochemistry of pure water in the presence of different gases is pretty well known. However, as soon as some solutes are added, many properties of the system are affected, as has been shown on salts, common "simple" solutes that can be considered as models to account for the composition of real sonochemical systems: the gas solubility decreases, the viscosity increases,[1] bubbles get smaller,[2] coalescence is reduced,[2a, 3] and probably the bubble dynamics is modified, too. Also the chemical activity has been shown to be impacted, though the reported trends show some discrepancy. Lepoint *et al.*[4] studied I_3^- yield (Weissler reaction) upon addition of $MgCl_2$ (in the concentration range from 10^{-4} M to 0.3 M) in CCl_4-saturated solutions sonicated by 1.67 MHz ultrasound under air. They reported a sharp minimum for concentrations between 2 10^{-3} M and 3 10^{-3} M and explained it by a change in the electrokinetic potential of the bubbles. However, this result could not be reproduced by Gutiérrez *et al.*[5] at 1 MHz under air saturated conditions, who obtained, both in the presence and absence of CCl_4 in solution, constant I_3^- yield up to a $MgCl_2$ concentration of 0.1 M or higher. At $MgCl_2$ concentrations higher than 0.1 M in CCl_4-saturated solutions (above 2 M in the absence of CCl_4) I_3^- yield then strongly decreased, which the authors correlated to the concomitant increase in viscosity creating conditions less favorable for cavitation. It is however to be noted that the change in viscosity is relatively

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low: at 20°C water viscosity is of 1 cP while that of 3 M NaCl is 1.2 cP.[1] On the contrary, some other works reported an increase in H_2O_2 or I_3^- formation rates upon addition of salts. For instance, Brotchie *et al.*[2a] measured 3-10 times higher I_3^- yields in concentrated solutions of $NaClO_4$ or $NaNO_3$ compared to water, during sonication at 515 kHz after saturation with He or Ar. They attributed it to lower dissolved gas concentrations leading to reduced gas and vapor contents in bubbles prior to collapse and to a lower clustering density. As for Katekhaye and Gogate,[6] they reported an increase by almost a factor of 2 of I_3^- yield during the sonication under air at 20 kHz or 204 kHz in the presence of 0.034-0.34 M NaCl or 0.029 – 0.29 M $NaNO_2$. The discrepancy that appears between the reported trends is probably to be accounted for by the lack of a detailed analysis of the various factors that can affect H_2O_2 or I_3^- formation. It is to be noted here that these two yields can also be different,[7] in particular in the presence of air, because KI dosimetry is not specific to OH radicals: the sonolysis of water in the presence of nitrogen yields nitrous acid[8] that readily oxidizes iodide ion[9] and this reaction is catalyzed by dissolved oxygen[10]. In particular, while these studies underlined the various physical effects induced by salts in solution, like changes in the viscosity or in the gas solubility, they did not take into account the chemical reactions in which salts can be involved.

Another source of information on the way salts impact the conditions of cavitation is sonoluminescence (SL). In air-saturated aqueous solutions of salts,[11] the SL spectra consist of a featureless continuum. On the contrary, in the presence of a rare gas, emissions arising from electronic transitions appear in the SL spectra: OH ($A^2\Sigma^+$-$X^2\Pi$) that is typical of aqueous solutions and emission from excited Na atoms accompanied by a blue satellite. The latter corresponds to the transition of a Na-Ar exciplex, an alkali-metal / rare-gas van der Waals molecule formed within the cavitation bubbles.[12] Lepoint-Mullie et al.[12] proposed the following mechanism of formation: after mechanical addition of some volume of solution to a collapsing bubble, the salt molecules would be released in the gas (or, actually, plasma) phase and homolytically cleaved. The metal atoms would then be electronically excited by three-body reactions, leading to Na^*. The formation of an electronically excited Na-Ar exciplex would occur following a three-body collision with two rare gas atoms.

Besides, recent literature showed that different bubble populations are responsible for the emissions of Na* and of the SL continuum. Abe and Choi[13] reported a difference in the timing distributions of both SL emissions during the sonication at 137 kHz of a NaCl 2 M aqueous solution saturated with Ar. Spectroscopy of SL indicated that the evolution of sonoluminescing bubble population and of Na-emitting bubbles with gas flow, power and frequency were different.[14] Moreover, visual observations of SL from both concentrated sulfuric acid solutions[15], phosphoric acid[16] and in aqueous solutions[13, 17] evidenced a spatial separation of continuum emission (and emission from OH radicals) and alkali-metal emission (blue continuum and orange Na* emission). The former was attributed to higher-temperature bubbles and the latter to lower-temperature bubbles.[13] It was also suggested, based on a bubble radius simulation that continuum emission would result from smaller bubbles than Na-atom emission. The latter assumption was confirmed by high-speed imaging in sulfuric acid at 23 kHz under Xe:[18] different cavitation bubble populations were observed in the zones of different SL colors, namely slow and spherically collapsing bubbles in the blue-emitting zones, fast bubbles subject to liquid jetting during their collapse in the red-emitting zone. However, while it is clear that Na^* emission arises only from jetting bubbles, it has also been reported in Xe saturated phosphoric acid that SL continuum emission can also be observed from large bubbles having a translational motion and therefore showing jetting.[19] Also, it should be kept in mind that not all sonochemically active bubbles do emit SL, whether

continuum or Na*. For instance, the spatial distribution of sonochemically active bubbles is broader than that of sonoluminescing bubbles.[20] Thus different kinds of bubbles (chemically active, SL-continuum emitting, SL-Na*-emitting, etc.) do coexist and they may be impacted in different ways by the presence of salts.

So, the common "simple" salts do in fact impact many aspects of acoustic cavitation, and the way to a global understanding of the effect of salts in cavitating systems necessitates a multi-lateral approach combining physical and chemical considerations. This paper aims at combining diverse complementary approaches (measurement of sonochemical activity, of sonoluminescence spectra and visualization of cavitation activity) to better understand the influence of the presence of a salt, using NaCl as a representative, in water under a rare gas flow system (He or Ar), at 362 kHz.

2. Experimental Methods

All chemicals (in particular NaCl, 99+%, STREM chemicals) were of analytical grade, and deionized water (Milli-Q 18.2 MΩ cm) was used to prepare all solutions. Argon, helium (99.999%) and Ar-20%O_2 gas mixture (99.9%) were provided by Air Liquide.

Experiments were performed at 362 kHz ultrasonic frequency and an absorbed acoustic power of 43 W in a thermostated glass cylinder fitted on the 362-kHz transducer (ELAC Nautik, 25 cm^2) which was connected to a multifrequency generator (T&C Power Conversion, Inc.). On top of the reactor, opposite to the high-frequency transducer was placed a 20-kHz titanium probe (750 W, 1 cm^2, Sonics generator), although not used here, to keep conditions constant with other studies in our group.

In the sonoreactor, 250 mL of the solutions were continuously sparged with Ar, He or Ar-20%O_2 at a flow rate of 70 mL/min for Ar and Ar-20%O_2 (respectively 210 mL/min for He) about 30 min before and during sonication. The solution temperature was maintained around 10°C with a Huber Unistat Tango cryostat.

The SL spectra were collected using parabolic Al-coated mirrors through the quartz window of the sonoreactor in the spectral range 240-800 nm using a SP 2356i Roper Scientific spectrometer (gratings 300blz300 and 150blz500, slit width 0.25 mm) coupled to a liquid-nitrogen-cooled CCD camera (SPEC10-100BR, Roper Scientific). For each experiment, at least three spectra (measured after reaching a steady-state temperature) were averaged and corrected for the background noise and for the quantum efficiencies of gratings and CCD. Optical high-pass filters were used when needed, to avoid second-order light. Typical spectrum acquisition times were of 60 s under Ar and 300 s under He.

Images of SL were taken through the same quartz window of the sonoreactor as SL spectra, using a digital camera (Canon EOS 70D) equipped with a Canon zoom lens of 35 mm. Acquisition was performed with the software Digital Photo Professional. Sensitivity was in general ISO 4000 and typical acquisition times were 10-300 s.

The formation rate of the gaseous sonolysis product H_2 was quantified for 1-h-sonolysis using a quadrupole mass spectrometer (PROLAB 300, Thermo Fisher) in multiple ion monitoring (MIM) mode, after trapping water vapor present in the outlet gas with molecular sieves (Aldrich, 3 Å). Mass spectrometer calibration was performed with gas mixtures provided by Messer. Hydrogen peroxide formation kinetics was monitored by UV−vis absorption spectrophotometry after the addition of 750 µL of a solution of 2×10^{-2} M $TiOSO_4$ in H_2SO_4

0.5 M to 750-µL samples of the sonicated solutions to form an orange Ti(IV) peroxide complex (λ_{max} = 410 nm, ε = 814 cm^{-1} mol^{-1} L). The accuracy for the reaction rate measurements was statistically estimated to be 10-20% for H_2 and 10% for H_2O_2, based on multiple frequent measurements of reference systems. In contrast to Weissler reaction, unless performed in the presence of a catalyst, this analytical method is specific to H_2O_2 and is not sensitive to secondary redox processes. To allow easier comparison with results published elsewhere, formation rates were converted into yields (in µmol/kJ) by multiplying them by the solution volume and dividing by the absorbed acoustic power.

The pH evolution during sonication was followed using a Cyberscan pH300 from Eutech Instruments. Presented H^+ yields were measured during approximately half an hour after reaching a steady-state temperature.

3. Results and discussion

3.1. Chemical yields

Fig. 1 presents sonolysis yields of H_2 and H_2O_2 (normalized to water) as a function of NaCl concentration, under Ar and He continuous flows. In both gases, the yields of H_2 and H_2O_2 decrease with an increase in NaCl concentration. A first possible explanation would consider a decrease in the number of active bubbles as a result of a decrease in gas solubility with an increase in salt concentration. This is in line with Okitsu et al.'s[21] observation that in pure water the chemical efficiency was proportional to the gas solubility of rare gases. Indeed, as shown in Fig. 1SI (in Supporting Information), H_2 and H_2O_2 yields divided by the gas solubility give the same value for He and Ar. It has also been shown that when salt is added in solution, the gas solubility decreases[22] leading to a lesser amount of coalescence,[2a] less active bubbles and lower sonochemical yields. However, this fact alone cannot account for the strong decrease in chemical yields: as exemplified in Fig. 1SI in Supporting Information, H_2 and H_2O_2 yields divided by the gas solubility decrease with NaCl concentration (H_2 seems to plateau above 2 M). Also, a decrease in water vapor pressure (of the order of 10% between 0 and 3 M)[23] alone cannot explain this strong decrease.

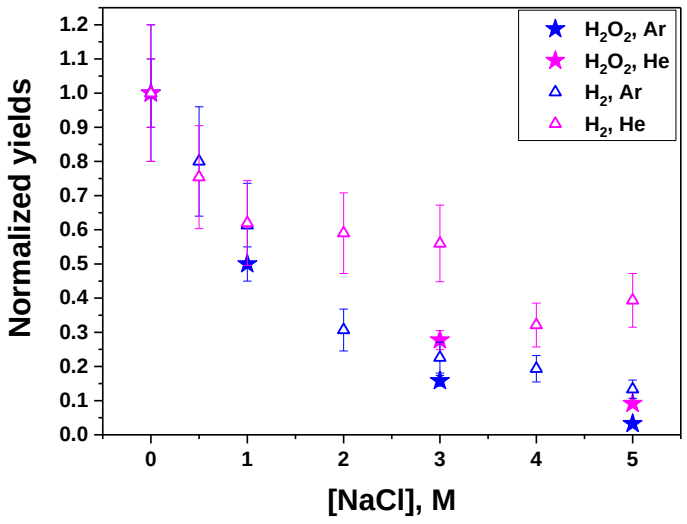


Fig. 1: Normalized yields of the sonolytical products H_2 and H_2O_2 as a function of NaCl concentration (362 kHz, 43 W, 13°C). Yields in pure water were of 0.40 µmol/kJ for Ar and 0.09 µmol/kJ for He.

One can suggest that chemical reactions do strongly contribute to this decrease in addition to the changes in the number of bubbles and vapor pressure. When solution droplets enter the cavitation bubbles during bubble collapse, salt molecules are released in the plasma following water evaporation, where they are homolytically cleaved, leading to $Na^{\cdot}$ and $Cl^{\cdot}$, as described by Lepoint-Mullie et al.[12]

$$NaCl))) \rightarrow Na^{\cdot} + Cl^{\cdot} \qquad (1)$$

The so-formed $Na^{\cdot}$ and $Cl^{\cdot}$ atoms can then react with H (or H_2), $OH^{\cdot}$ and H_2O species, hence impacting the formation yields of sonolysis products. Reactions with water molecules (3 and 8) are expected to be prevailing due to the higher concentration and reactive cross-section of these molecules, but many possible reactions do coexist, the reaction rates of which strongly depend on whether the considered species are in their ground or excited state.[24] Some of the relevant reactions are (with M a third body):

$$Na^{\cdot} + OH^{\cdot} \rightarrow NaOH \qquad (2)$$

$$Na^{\cdot} + H_2O \rightarrow NaOH + H \qquad (3)$$

$$Na^{\cdot} + H + M \rightarrow NaH + M \qquad (4)$$

$$Cl^{\cdot} + OH^{\cdot} \rightarrow HOCl \qquad (5)$$

$$Cl^{\cdot} + H \rightarrow HCl \qquad (6)$$

$$Cl^{\cdot} + H_2 \rightarrow HCl + H \qquad (7)$$

$$Cl^{\cdot} + H_2O \rightarrow HCl + OH^{\cdot} \qquad (8)$$

$$Na^{\cdot} + Cl^{\cdot} + M \rightarrow NaCl + M \qquad (9)$$

As underlined previously, no agreement is found in the literature concerning the influence of salts on H_2O_2 formation rate. The observed discrepancy may be traced back to chemical reactions linked to the nature of the used salts. For instance, contrary to the present work, Katekhaye and Gogate[6] reported an increase in Weissler reaction rate in the presence of NaCl during the sonication of a KI solution at 20 kHz under air. They attributed it to a change in the physicochemical properties of the solution due to the salt, leading to increases in collapse pressure and temperature and thus to higher H_2O_2 formation rate. However, this increase in I_3^- formation can most probably be attributed to the following interfering reaction:

$$Cl^{\cdot} + I^- \rightarrow Cl^- + I^{\cdot} \qquad (10)$$

The so-formed $I^{\cdot}$ atom can then lead to I_3^- formation following the same reaction path as in standard Weissler reaction. In this case, no direct correlation can be considered between I_3^- and H_2O_2 yields. Similarly, the presence of an interfering reaction can explain the increase in H_2O_2 formation rate observed by Brotchie *et al.*[2a] upon addition of $NaClO_4$ or $NaNO_3$ during sonication under He or Ar at 515 kHz. Indeed, the sonolysis products of ClO_4^- and NO_3^- anions are oxidants that can lead to the formation of additional H_2O_2. For instance, it was shown[25] that the reaction of NO_3^- with $OH^{\cdot}$ radicals forms $NO_3^{\cdot}$ radicals that yield H_2O_2 after hydrolysis, thus doubling the amount of H_2O_2 produced as soon as enough NO_3^- ions are present.

The mechanism of scavenging of $OH^{\cdot}$ radicals and $H^{\cdot}$ atoms by $Cl^{\cdot}$ and $Na^{\cdot}$ proposed here explains the concomitant decrease in H_2 and H_2O_2 yields. Due to the formation of HCl

(reactions 6, 7, 8) and NaOH (reactions 2, 3), a change in the pH of NaCl solutions may be expected during sonication in a rare gas atmosphere (in contrary to water sonolysis under Ar or He, where no pH change is to be observed). Indeed, as shown in Fig. 2SI (in Supporting Information) that presents the concentration with sonication time of sonolytically produced H^+ in a 3 M NaCl solution under He, acidification of the solution occurs. The reason why more HCl than NaOH is produced may be due to the competition for reaction with OH radicals (reactions 2&5) and different reactive cross-sections of the different reactions. Yields of H^+ for the different NaCl concentrations and the two gases are presented in Fig. 2.

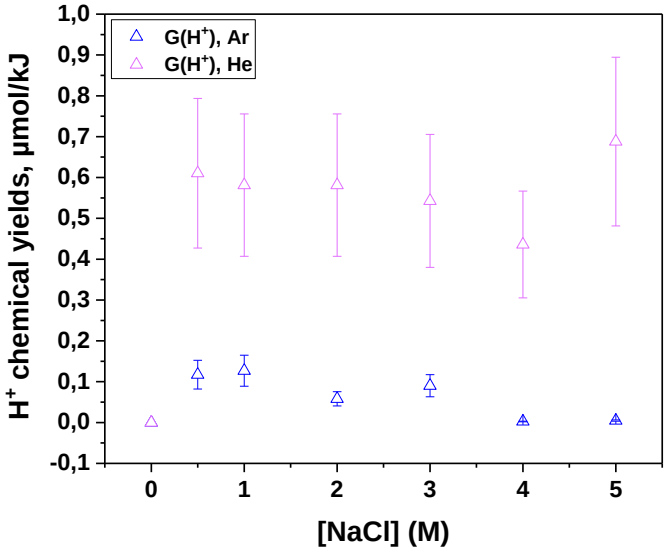


Fig. 2: Yields of H^+ formed during the sonolysis of NaCl solutions under Ar or He (362 kHz, 43 W, 13°C).

The most striking feature in Fig. 2 is the very large H^+ yields obtained under He: much higher (an order of magnitude) than yields of water sonolysis products H_2 and H_2O_2 in NaCl solutions saturated with He (Fig. 1) on the one hand, and on the other hand, much higher than H^+ yields under Ar. The H^+ can a priori be formed via reactions 6, 7 and 8. The first two involve H atoms or H_2 molecules and directly lead to a decrease in H_2 formation. Comparison of H^+ yields under He with a decrease in H_2 yields (compared to the water case (Fig. 3)) shows that the decrease in H_2 formation yield under He cannot account for the very high proton yields, thus underlining the importance of reaction 8 in the proton formation. This pH evolution shows one of the very rare examples (if any other exists) where a "sonochemical activity" would be higher under He. This surprising fact may be traced back to the different bubble contents induced by the different gas solubilities (the number of Ar atoms inside bubbles is higher than in the He case) and to the larger reactive cross-section of Ar compared to He due to the atom larger size. Thus, while under He, reactions 6-8 of radicals are favored, in the Ar case three-body reactions like reaction 9 have a high probability.

Another interesting feature in Fig. 2 is that the effect of NaCl concentration (in the range 0.5-5 M) is different for both gases. Under He, $G(H^+)$ is nearly independent from NaCl concentration, while under Ar, it decreases. Actually, acidification occurs due to the presence of NaCl, thus the relevant parameter to consider would be H^+ yield relative to salt concentration (Fig. 3SI in Supporting Information) that decreases for both gases, though with a stronger decrease for Ar. As already stated, the origin of the changes in yields of sonochemical products in the presence of salt is not only based on reactions 2-8, but also

linked to a decrease in the number of chemically active bubbles with NaCl concentration. The change in gas solubility between water and 5 M NaCl aqueous solution is almost double for Ar than for He (3.9 vs. 2.1)[22], which may lead to a stronger decrease in the active bubble population for Ar, and thus participate (as confirmed by Fig. 1SI) in the more pronounced decrease in H_2 and H_2O_2 yields with NaCl concentration (Fig. 1) and of the relative H^+ yield.

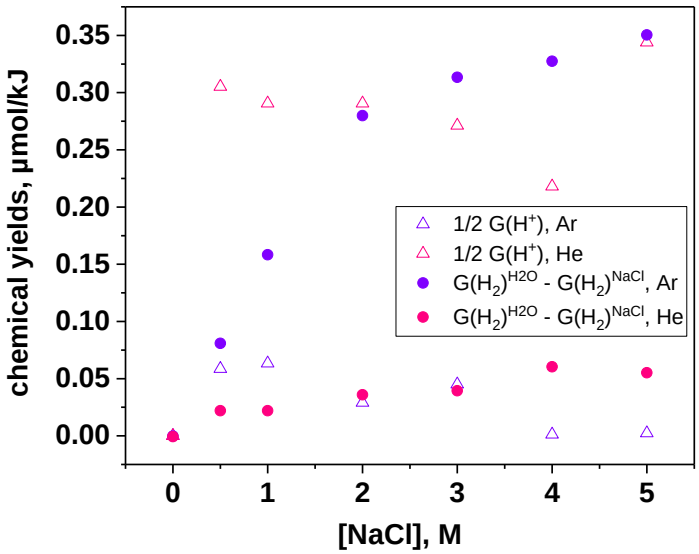


Fig. 3: Comparison of the yields of H^+ ($G(H^+)$) formed during the sonolysis of NaCl solutions under Ar or He (362 kHz, 43 W, 13°C) with a decrease in H_2 yields between water and NaCl solutions ($G(H_2)^{H2O}$-$G(H_2)^{NaCl}$).

3.2. Sonoluminescence spectra

Fig 4 shows SL spectra obtained under Ar, in water and in 1 M and 3 M NaCl solutions. They show the typical SL continuum, emission from excited OH radicals (in particular, OH ($A^2\Sigma^+$-$X^2\Pi$) transition around 310 nm) and a very intense Na^* line accompanied by a blue satellite corresponding to Na-Ar^* exciplex.[12] To increase light input inside the spectrophotometer, its slit was opened to 0.25 mm, which decreases the spectral resolution. Therefore, Na^* doublet is not distinguished, neither the peak broadening due to interaction with the bubble content (broadening that was studied in details elsewhere[26]).

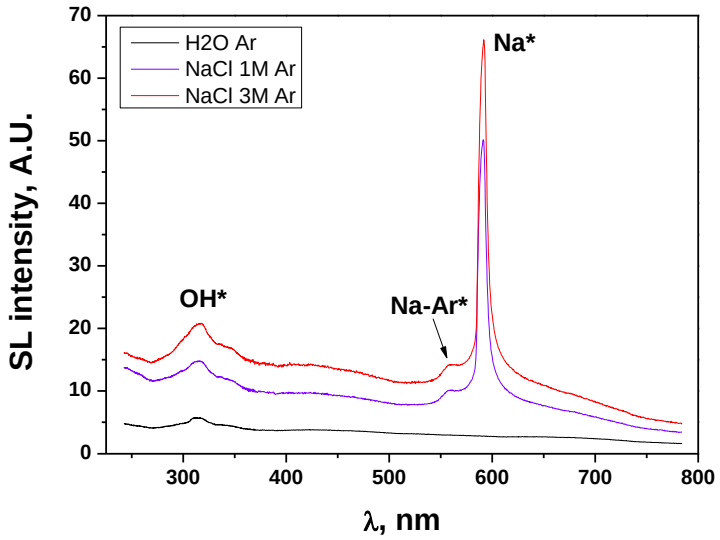
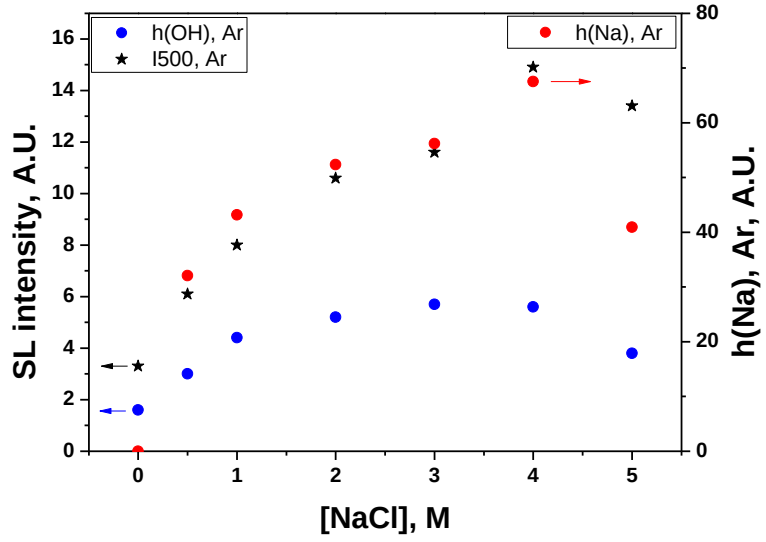


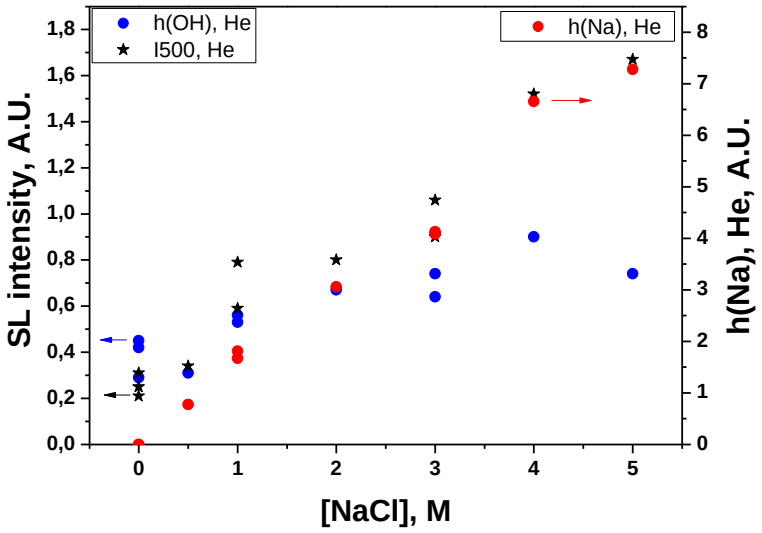
Fig. 4: Measured SL spectra under Ar flow, in water and in 1 M and 3 M NaCl aqueous solutions (362 kHz, 43 W, 10°C).

Similar spectra were obtained under He (Fig.4SI), though with a lower total intensity and a less intense Na^* peak relatively to the continuum. The lower SL intensity under He is well documented in the literature[27] and has been attributed to several factors: He lower solubility[28] leading to fewer active bubbles, higher thermal conductivity[28] and higher ionization potential.[29] As for the intensity of Na^* peak relatively to the continuum, it will be discussed below.

Three parameters were quantified in these spectra: the continuum intensity, measured at 500 nm, the intensity of OH ($A^2\Sigma^+$-$X^2\Pi$) emission, defined as the difference between OH peak intensity at its maximum and continuum intensity at 360 nm, and the intensity of Na* emission, taken at 590 nm after subtraction of a linear baseline between 500 and 700 nm. Their evolution with NaCl concentration is presented in Fig. 5.



a)



b)

Fig. 5: Evolution with NaCl concentration of the SL continuum intensity, taken at 500 nm, of OH ($A^2\Sigma^+$-$X^2\Pi$) transition emission intensity and of Na^* line intensity, for Ar (a) and He (b).

Under Ar flow, these intensities show a fast increase up to approx. 1-2 M, then a slower increase between 2 and 4 M. They finally decrease above 4 M. Similarly, under an air flow and at 515 kHz, Wall *et al.*[11] observed an increase of the SL continuum intensity up to 3 M NaCl, then a sudden decrease. Under He flow, while the intensities of SL continuum and of Na^* line show a fast linear increase, that of OH emission is less pronounced. This fact may be explained by a change in bubble content: indeed, He solubility decreases with NaCl concentration, leading to a lower He concentration in bubbles. Moreover, according to Storey and Szeri,[30] a decrease in He content should lead to a decrease in water vapor mobility and an increase in the amount of water vapor trapped. The resulting change in composition must affect the conditions reached at collapse (on the one hand, more water molecules provide more material to produce OH radicals, on the other hand these molecules will cushion collapse and limit the energy concentration), conditions that control the extent of excited OH radical formation. The resulting effect is a slower increase in OH emission intensity.

The presence of a high salt concentration also decreases water vapour pressure, which would favor a higher SL intensity. However, this decrease is only about 10% between 0 & 3 M NaCl, i.e., equivalent to a decrease caused by a 2°C change in the bulk temperature. The latter leading to an increase in SL intensity of less than 20%,[27] it cannot account for the very large increase observed here.

It is usually considered that SL would follow the same trend as sonochemical activity. Though, it is observed here that upon addition of NaCl, the yields of H_2 and H_2O_2 decrease, while the SL intensity increases. This can however be easily explained if one considers the different bubble populations that coexist. Of all chemically active bubbles, only some emit SL.[20, 31] Besides, among the former, only some are subject to jetting and solution droplet injection that leads to chemical reactions (2-9). Interestingly, one work[32] already reported changes in experimental conditions leading to opposite trends in sonochemical activity and SL intensity. Thus, some changes in the experimental conditions, such as the salt concentration and subsequently the amount of dissolved gas, can lead to a global decrease in the active bubble population but at the same time lead to conditions more favorable to SL

(e.g. less perturbations allowing a more symmetrical collapse), which strongly increases the proportion of SL bubbles within the active bubble population.

Fig. 6 exemplifies the evolution of the SL continuum intensity (normalized to water to allow an easier comparison) with the gas solubility for Ar, He and air (for the latter, literature[11] values were taken). For all three gases, the lower the gas solubility (except at the lowest solubilities for air), the higher the SL continuum intensity, but the slope obviously depends on the gas nature and is much larger for He for which the intensity of the SL continuum increases by almost a factor 7 between water and NaCl 5 M. Other factors that do enhance the increase in the SL continuum intensity are the decreasing water vapor pressure and the increase in the acoustic pressure felt by the sonoluminescing bubbles (due to the lower attenuation of the acoustic wave).

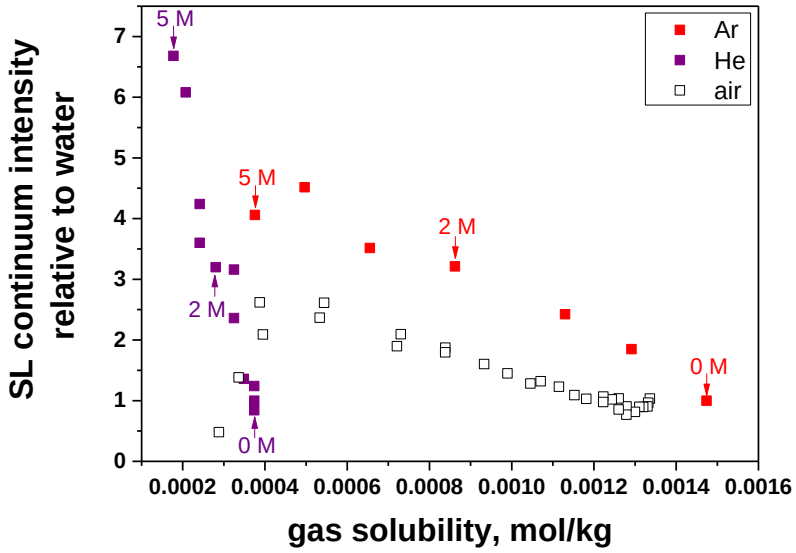


Fig. 6: Evolution of the SL continuum intensity (normalized to water) with the gas solubility for Ar, He and air (for air: literature values[11]).

Let us now consider jetting Na^*-emitting bubbles. To quantify the efficiency of excitation, the intensity of Na^* emission is normalized by NaCl concentration. As exemplified in Fig. 7, the observed trend depends on the rare gas nature. The comparison cannot be performed with air, since in this case no Na^* emission is seen.

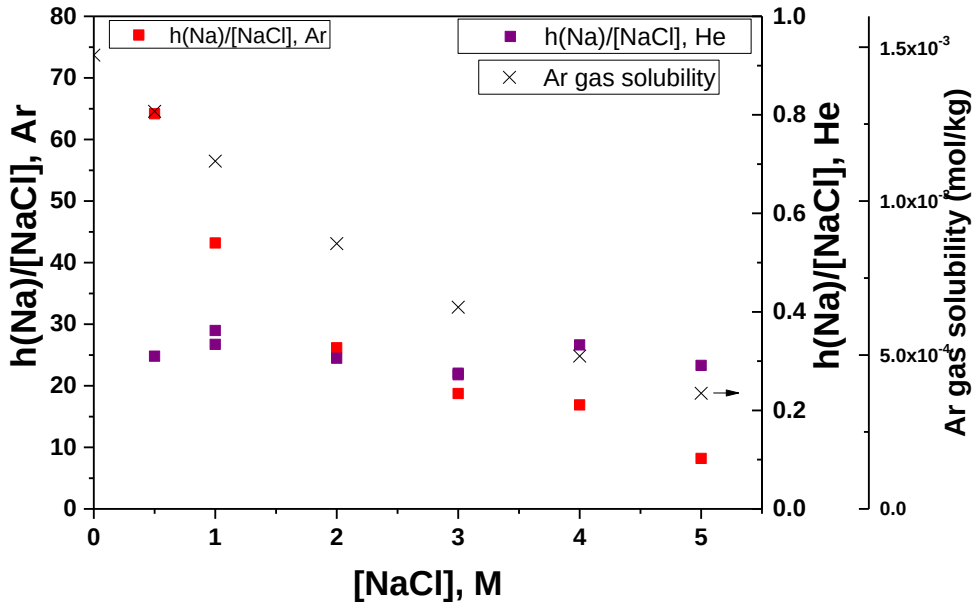


Fig. 7: Evolution with NaCl concentration of Na^* line emission relative to NaCl concentration (A.U.), under He and Ar flows (values corrected to consider the same spectral acquisition time of 60 s), and of Ar solubility (He solubility is given in Fig. 5SI).

Independent of the NaCl concentration, higher values of the intensity of Na^* emission normalized by NaCl concentration are obtained for Ar, and correlate with the stronger decreases in H_2 and H_2O_2 yields in NaCl solutions under Ar. These higher values under Ar cannot be explained by the higher solubility of Ar: indeed He solubility in NaCl 0.5 M is close to Ar solubility in NaCl 5 M, while the corresponding intensities of Na^* emission normalized by NaCl concentration are very different. A plausible explanation is the larger bubble radius under Ar,[2] particularly for [NaCl] $\leq$ 2 M, larger size that may favor jetting and droplet injection. Direct observations with a high-speed camera would be needed to confirm this assumption but are pretty hard at high US frequency. Also, one may expect a higher probability of Na^* formation for each bubble in the Ar case.

Another striking difference in Fig. 7 is that Na^* emission intensity is proportional to NaCl concentration under He flow (which is the *a priori* expected behavior under the assumption of a constant jetting bubble population) but clearly not under Ar. This means that the number of jetting bubbles is approximately constant under He (in spite of He decreasing solubility) but not under Ar. In the Ar case, the higher the salt concentration is, the lower the relative Na^* emission and this decrease is larger than would be expected from the evolution of the gas solubility (Fig. 7). This difference in the evolution of Na^* emission normalized intensity between Ar and He correlates with the observed trends in H_2 yields (Fig. 1): while it is roughly linear in He, it shows an inflexion in Ar for 2 M NaCl, i.e. at the concentration for which an inflexion point is observed in the intensity of Na* relative emission. This correlation between the evolutions of Na* relative emission intensity and of H_2 yield decrease confirms the role of chemical reactions 2-8 in the quenching of H and H_2.

Another hypothesis to investigate to explain the decrease in the relative Na^* emission under Ar would be quenching of Na^* excited state. The most probable way of quenching Na^* would be to oxidize it back to Na^+, for instance by reaction with OH radicals. To test this

possibility, SL spectra of a 1 M NaCl solution were measured under a gaseous mixture of Ar and 20% O_2, and under Ar in the presence of 0.1 M H_2O_2 in solution. In the first case, oxidants are present mostly inside bubbles, in the latter in solution. As shown in Fig. 7, in both cases the intensity of Na* emission is hardly changed compared to the reference Ar case, meaning that no pronounced quenching occurs. The main differences observed are a large increase of the SL continuum intensity in the presence of O_2, in full agreement with the literature[33], and absorption by H_2O_2 of the UV part of the SL spectrum. This comparison confirms that the decrease in the relative Na emission under Ar is most probably caused by a decrease in the number of Na^*-emitting bubbles (i.e. jetting bubbles).

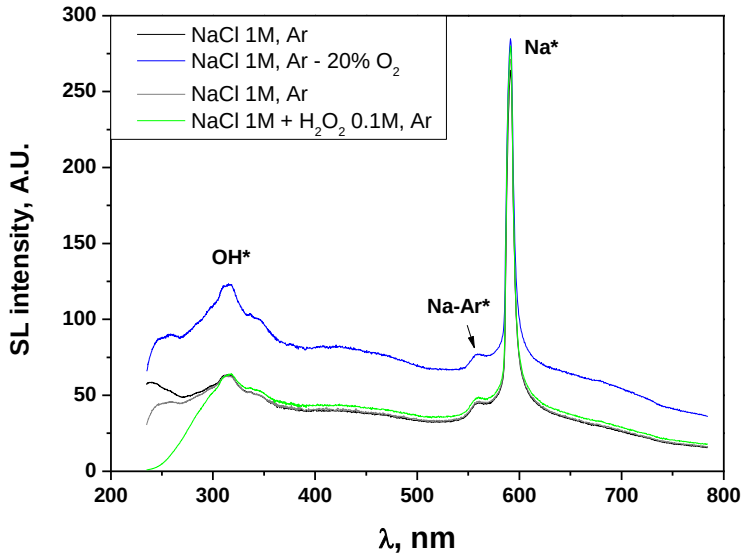


Fig. 8: SL spectra of a 1 M NaCl solution under Ar, Ar-20% O_2 and Ar after addition of 0.1M H_2O_2.

The spectra in Fig. 8 are also in agreement with the mechanism of formation of Na^* by homolytical dissociation of NaCl proposed by Lepoint-Mullie et al.[12] Indeed, this mechanism does not imply direct reduction of Na^+ so that formation of Na^* is not sensitive to the presence of oxidants.

To further investigate the effect of salt for both rare gases, it is interesting to look at the relative evolutions of the different populations of bubbles: the bubbles emitting SL continuum and the jetting Na^*-line emitting bubbles. In this view, Fig. 9 presents Na line intensity normalized by NaCl concentration, relative to the continuum intensity.

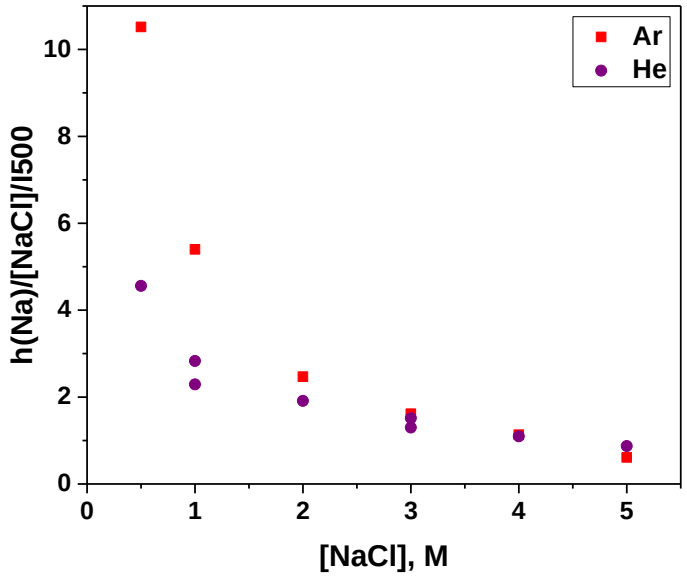


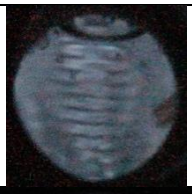
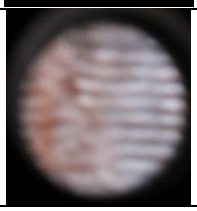
Fig. 9: Evolution with NaCl concentration of Na^* line intensity normalized by NaCl concentration, relative to the continuum intensity, taken at 500 nm, under He and Ar flows.

Two striking features appear in Fig. 9. First, for NaCl concentrations ≤ 2 M this ratio takes higher values under Ar, in agreement with the literature,[14] indicating that for a given SL continuum emission, more bubbles are producing droplet injection and Na^* emission under Ar. This fact may be explained by Ar higher solubility that leads to a higher number of bubbles and therefore more interactions between them, and to the bigger bubble radius under Ar,[2] that may favor jetting and droplet injection. Differences in bubble dynamics may also be conceivable, as was observed for instance between Ar and air:[14] larger Ar bubbles left a trace of smaller bubbles behind, which was not observed in air. This different behavior may account for the absence of Na^* emission in air.[14] Second, this ratio strongly decreases upon addition of salt, with a more pronounced decrease under Ar, leading to similar values for both gases at concentrations ≥ 2 M.

3.3. Visualization: photographs of SL

Table 1 presents photographs of SL taken through the window of the reactor during the sonication at 362 kHz of NaCl aqueous solutions of different concentrations, under continuous Ar or He flow. Optics were focusing onto the central zone of the reactor, below the sonotrode. The tip of the latter can be distinguished in the last two rows of the table. In some pictures, a big bubble is present at the top. It has however no impact on cavitation and on observations made since it is stuck in the window holder, not in the zone of interest.

Table 1: Photographs of SL of NaCl solutions of different concentrations, under continuous Ar or He flow. Under He for water and 1 M NaCl, the light was too dim for a proper picture to be taken. The “shadow” sometimes present on the window is due to water condensation.

[NaCl], M	Acquisition time, s Ar / He	Pictures of SL, Ar	Pictures of SL, He
0	180 / -		-
1	120 / -		-
3	10 / 300		
4	10 / 300		
5	10 / 300		

A clear spatial separation can be observed between SL continuum (blue) and Na line (orange) emissions, in agreement with observations reported in the literature.[13, 15a, 17] In general, these pictures illustrate the tendencies observed in SL spectra: a much less intense light under He (therefore longer acquisition times were used), a strong increase of both continuum and Na line intensities with NaCl concentration under He, while these increases end at 4 M NaCl under Ar. For 5 M NaCl under Ar the photography even appears less red than blue, corresponding to the stronger decrease in Na line intensity compared to the continuum intensity.

At low (0-1 M) salt concentration under Ar, a standing wave pattern is visible only locally, below the sonotrode tip, and due to reflection of the ultrasonic wave on it. It starts appearing in the whole cavitation zone at 2-3 M NaCl and gets better defined with further increase in the salt concentration. This evolution is due to the strong decrease in gas solubility with NaCl concentration, that leads to the formation of much less (big) degassing bubbles, that otherwise dampen the propagation of the acoustic wave.[34] For both gases, the formation of a standing wave correlates with the evolution of Na^* emission intensity normalized by NaCl concentration (Fig. 7). For He, the solubility of which is always low, the standing wave is expected to be formed also at 0-3 M NaCl where no photos could be taken. For Ar on the

contrary, the standing wave is seen only above 2 M NaCl: between 0-2 M, only a low percentage of standing wave is present, and very high relative intensities of Na emission are observed; while this percentage strongly increases (up to 2 M) the decrease in the relative emission of Na^* is fast; above 2 M a strong standing wave is formed, much lower relative intensities of Na emission are observed and the decrease of the latter slows down. Thus the presence of a standing wave strongly penalizes droplet injection and Na^* emission. This observation is in agreement with the reported (opposite) effects of a gas flow: a high Ar gas flow rate favors collisions, merging and splitting of bubbles, hence Na^* emission.

On the other hand, the standing wave, getting stronger as the dissolved gas concentration decreases, favors symmetrical collapse of bubbles and therefore SL continuum emission, which contributes to the decrease in the normalized Na^* line intensity relative to the continuum intensity (Fig. 9).

4. Conclusion

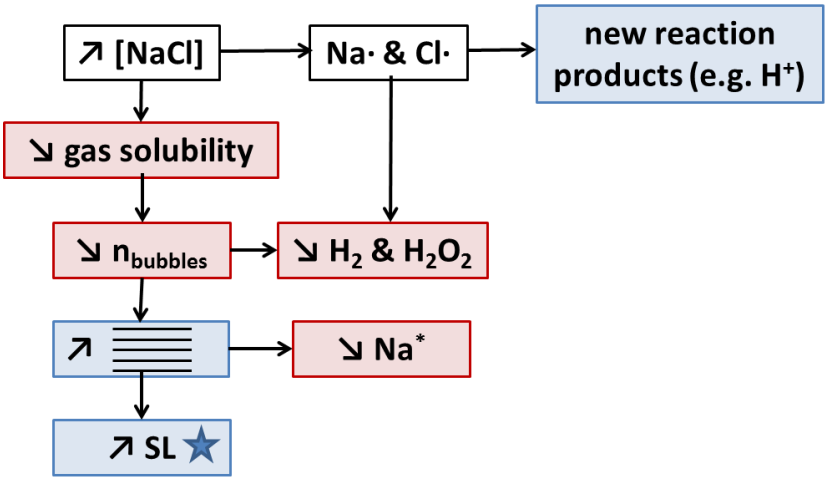


Fig. 10: Schematic representation of the different impacts of salt on sonochemistry and sonoluminescence.

The presence of a high NaCl concentration in aqueous solutions strongly affects the yields of sonochemistry and sonoluminescence, as summarized in Fig. 10. A decrease in H_2 and H_2O_2 yields was confirmed, and attributed to the combination of physical and chemical effects: the decrease in gas solubility combined to an increase in solution viscosity leads to changes in the number of chemically active bubbles; besides, in bubbles undergoing asymmetric collapse, $Na^{\cdot}$ and $Cl^{\cdot}$ radicals can form and react with H and $OH^{\cdot}$ radicals. The opposite trends in H_2O_2 yield obtained in some previous works could be explained by chemical reactions between the salt and the water sonolysis products or between the salt and iodide ions. This remark underlines the fact that even in very simple systems, care should be taken that H_2O_2 or H_2 yields cannot always be considered as an accurate measurement of the sonochemical activity. Indeed, these species can further react, or H and $OH^{\cdot}$ radicals can be scavenged before forming them. It was also shown that $Na^{\cdot}$ and $Cl^{\cdot}$ radicals can react with water molecules in the collapsing bubbles, and that the balance of all reactions of these radicals leads to an acidification of the solution. Interestingly, H^+ yield gets higher under He

than Ar for concentrated salt solutions showing one of the very rare examples of a higher sonochemical activity under He.

A good correlation is obtained between the sonochemical activity and Na^* emission in SL spectra arising from 'jetting' bubbles. Indeed, a stronger Na^* emission is observed under Ar compared to He, concomitant to a stronger decrease in yields of sonolytical products. Moreover, it was shown that the formation of a standing wave (for concentrations above 2 M under Ar) is unfavorable for droplet injection and $Na^{\cdot}$ reactions (resp. Na* emission).

In general, sonoluminescence continuum intensity increases with salt concentration, due to the decrease in gas solubility that leads to less coalescence, less damping of the ultrasonic wave and to the formation of a standing wave. All these effects favor an increase in the number of sonoluminescing bubbles, at least up to a certain point. Indeed, above 4 M in Ar, a decrease in SL continuum intensity is observed, concomitant with a decrease in Na^* emission and with very low yields in sonolytical products. A similar decrease in the SL continuum intensity was also observed under air above 3 M.[11] This sudden decrease might be related to the dissolved gas concentration getting too low to allow the formation of enough active bubbles, although the threshold depends on the dissolved gas nature and isn't even detected up to 5 M NaCl under He, the gas with the lowest solubility among the studied three. This property of He may be linked to its very high diffusion coefficient that would favor bubble formation and growth.[2b]

This work underlines that three levels are necessary to contempt salt effect: the impact it has in each bubble (e.g. due to chemical reactions and changes in water vapour pressure), on the bubble number (e.g. because of changes in the gas solubility), and on the different bubble populations (e.g. due to the formation of a standing wave). While the total number of chemically active bubbles decreases upon addition of salt, the proportion of SL bubbles strongly increases due to more favorable conditions. As for the number of Na^*-emitting bubbles, it seems to be constant under He but strongly decreases under Ar. Thus, the very simple NaCl salt appears to have a complex effect on sonicated solutions.

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