

Squeezing Alcohols into Sonoluminescing Bubbles: The Universal Role of Surfactants

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We conduct an experimental study of the dependence of single bubble sonoluminescence intensity on the concentration of various alcohols. The light intensity is reduced by one-half at a molar fraction of ethanol of $\approx 2.5 \times 10^{-5}$; butanol achieves the same reduction at a concentration 10 times smaller. We account for the results by a theoretical model in which the alcohols are assumed to be mechanically forced into the bubble at collapse, modifying the adiabatic exponent of the gas. The increasing hydrophobicities of the alcohols lead to decreasing effective adiabatic exponents, and thus to less heating and therefore less light. Support for this model is obtained by replotting the experimental light intensity values vs the calculated exponents, yielding a collapse of all data onto a universal curve.

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In 1990 Gaitan [1] discovered that a single air bubble trapped in an acoustical field can emit bursts of light so strong as to be visible to the naked eye. During recent years extensive theoretical and experimental research has been done in this field, and now the basic mechanisms of this so-called single bubble sonoluminescence (SBSL) seem to be resolved [2–17]. The parameter regime of SBSL is set by the shape stability of the bubble [3–5], its diffusive stability [3,18], and its chemical stability [8,12,13]. The light seems to originate from thermal bremsstrahlung [10,11,16,17], induced by (nearly) adiabatic heating of the bubble in the final stages of the radial collapses induced by the acoustic driving.

Inspired by the experimental finding that one drop of alcohol can extinguish SBSL [19,20] and by the study on the effect of alcohols in multibubble sonoluminescence (MBSL) by Grieser's group [21,22], we experimentally study the influence of various alcohols on SBSL in the present paper.

A SBSL bubble was created in a spherical flask containing purified water, driven by two piezotransducers at a frequency of 35 kHz. Degassing of the dissolved air was achieved through boiling. The oxygen concentration was directly monitored through oxyometry from which the argon concentration that is the relevant one in SBSL [8] can easily be found. The light from the bubble was focused onto a high-sensitivity photodiode. The resulting photocurrent signal was amplified, digitized, and read out by a computer.

Small amounts of different alcohols (ethanol C_2H_5OH , 2-propanol C_3H_7OH , and 1-butanol C_4H_9OH) were added. Subsequent stirring was necessary because of the long diffusive time scale of alcohol in water ($\tau_{diff} = R_{flask}^2/D \approx 29$ days with the flask radius $R_{flask} = 5$ cm and the typical diffusion constant $D \approx 10^{-5}$ cm²/s of the above-mentioned alcohols in water). The driving frequency must

be close to a resonance frequency of the flask in order to obtain high driving pressures and therefore SBSL. Adding a small liquid volume detunes the resonator, so that small adjustments of the driving frequency (≈ 10 Hz) were necessary in order to keep the driving pressure constant (at the peak of the resonance). Possible effects of this adjustment of resonance frequency were checked by adding an equal amount of water instead of alcohol. No intensity changes were observed in this case.

The light intensity as a function of the bulk molar fraction of alcohol n_b is seen in Fig. 1. Tiny amounts of alcohol strongly decrease the intensity in all cases. The effect is more pronounced the longer the carbon chain of the alcohol: for butanol a 10 times smaller concentration is sufficient to halve the light intensity; see Table I.

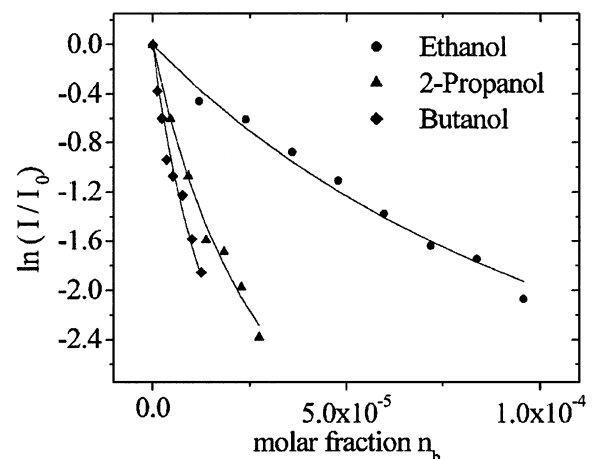


FIG. 1. Logarithmic plot of the normalized SBSL light intensities vs bulk alcohol concentration n_b . The symbols refer to measurements with different alcohol species. The solid lines show fits according to Eq. (5). Note that the dependence $I(n_b)$ is in general *not* exponential, but approaches exponential decay for very small n_b .

TABLE I. Characteristic parameters of the intensity data. $n_b[I(0)/2]$ is the measured bulk alcohol concentration at which the SL intensity is halved, f_{alc} the number of degrees of freedom. A_{alc} results from the fit Eq. (5) to the data and $A_{\text{alc,th}}$ from theory. r_{dif} is obtained from Eq. (9). The change in surface tension with n_b and the vapor pressure of the pure substance (last two columns) are material parameters taken from Refs. [28,29] (for a temperature of 25 °C).

Alcohol	$n_b[I(0)/2]$	f_{alc}	A_{alc}	$A_{\text{alc,th}}$	r_{dif}	$\frac{\partial\sigma}{\partial n_b}/\text{gs}^{-2}$	p_v/kPa
Ethanol	2.6×10^{-5}	48	475	564	14.9	-1213	7.87
Propanol	5.3×10^{-6}	66	1568	1681	4.2	-3614	2.76
Butanol	2.7×10^{-6}	84	1920	4190	1.3	-9007	0.86

Qualitatively, Ashokkumar *et al.* [21] observe the same trend in MBSL, but at considerably larger alcohol concentrations, with half-intensity concentrations of $n_b \approx 2 \times 10^{-3}$ (ethanol) and $n_b \approx 1 \times 10^{-4}$ (butanol). They postulate [21] that the hydrophobic alcohol molecules accumulate at the bubble surface, are then forced inside during bubble collapse, and there quench the light emission. The surface accumulation will be stronger for longer carbon chains. Our work picks up these ideas for the SBSL case with some modifications, and proceeds to develop a quantitative model. The calculation of the expected light intensity within our theory can be subdivided into four steps.

(i) *Molar fraction $n_g(n_b)$ in the gas bubble.*—The alcohol bulk concentration n_b determines the molar alcohol fraction n_g inside the bubble. This dependence is, in general, nontrivial, with hydrophobicity, vapor pressure, surface tension, and even the bubble dynamics itself factoring in [23]. For low concentrations, however, we can assume a linear dependence,

$$n_g = A_{\text{alc}} n_b, \quad (1)$$

with an alcohol dependent fit parameter A_{alc} . Later we will theoretically calculate A_{alc} , finding good agreement with the fit results.

(ii) *Adiabatic exponent $\gamma(n_g)$ of the alcohol-argon mixture.*—After the alcohol has been squeezed into the bubble, it basically contains a mixture of argon, which accumulates in sonoluminescing air bubbles [8], and the vapor of the employed alcohol. The effective adiabatic exponent of the mixture can be derived from Dalton's law,

$$\gamma(n_g) = \frac{n_g(f_{\text{alc}} + 2) + (1 - n_g)(f_{\text{Ar}} + 2)}{n_g f_{\text{alc}} + (1 - n_g) f_{\text{Ar}}}. \quad (2)$$

Here, $f_{\text{Ar}} = 3$ and f_{alc} indicate the number of degrees of freedom of argon and alcohol, respectively. As temperatures inside a collapsing SBSL bubble very likely correspond to energies of 1–2 eV [16], while typical energies for vibrational quanta are ≤ 0.1 eV (those of rotational quanta are even 2 orders of magnitude smaller), we can safely assume that all degrees of freedom are available. Thus, $f_{\text{alc}} = 6 + 2(3N - 6)$, where N is the number of atoms in the molecule. Note that γ in (2) will only slightly change in the early stages of heating of the bubble, when the alcohol molecules begin to dissociate, as γ depends only on the product $n_g(f_{\text{alc}} - 3)$, and $f_{\text{alc}} \gg 1$: For example, dissociation in two products of about equal size

roughly halves the number of degrees of freedom of each but doubles n_g .

(iii) *Maximum temperature $T_{\text{max}}(\gamma)$ in the bubble.*—SBSL light emission has been explained satisfactorily as thermal bremsstrahlung of the (nearly) adiabatically heated gas inside the bubble [10,11,16,17]. Calculations coupling bubble dynamics with heat exchange have shown [24] that the gas inside the bubble maintains the ambient temperature most of the time. Only at collapse it is heated adiabatically for a brief time. To keep the model simple, we will replace the actual change in thermal coupling by an abrupt crossover from isothermal to adiabatic behavior at a certain bubble radius R_{ad} . From R_{ad} , the bubble is assumed to adiabatically collapse down to R_{min} , which is very close to the van der Waals hard core radius h . From the van der Waals equation of state, we therefore have

$$T_{\text{max}}(n_g) \propto \left(\frac{R_{\text{ad}}^3 - h^3}{R_{\text{min}}^3 - h^3} \right)^{\gamma(n_g)-1}. \quad (3)$$

As *a priori* we do not know the length ratio $B_{\text{alc}} \equiv [(R_{\text{ad}}^3 - h^3)/(R_{\text{min}}^3 - h^3)]^{1/3}$, it is the second fit parameter of the model.

(iv) *Light intensity $I(T_{\text{max}})$.*—References [10,11,16,17] show that the light intensity I (as a function of the temperature) is essentially obtained as the product of two factors: (a) blackbody radiation according to the actual temperature of the bubble ($\propto T^4$), and (b) the finite opacity of the bubble (dominated by a factor $\propto \exp(-E_{\text{ion}}/2k_B T)$, E_{ion} being the ionization energy of argon and k_B the Boltzmann constant). The relative intensity reduction due to the addition of alcohol is thus approximately

$$\frac{I(n_g)}{I(0)} = \left[\frac{T_{\text{max}}(n_g)}{T_{\text{max}}(0)} \right]^4 \times \exp \left[-\frac{E_{\text{ion}}}{2k_B} \left(\frac{1}{T_{\text{max}}(n_g)} - \frac{1}{T_{\text{max}}(0)} \right) \right]. \quad (4)$$

We now plug the four elements of the model together and obtain a well-defined function of light intensity vs n_b ,

$$\frac{I(n_b)}{I(0)} = F(n_b, f_{\text{alc}}, A_{\text{alc}}, B_{\text{alc}}), \quad (5)$$

with two fit parameters A_{alc} and B_{alc} to which we have attributed physical meaning above. The nonlinear fit (5) indeed describes our data sets very well; see Fig. 1. Furthermore, we find that the parameter B_{alc} is virtually the

same for all alcohols (it varies by about $\pm 10\%$ around $B_{\text{alc}} = 1.3$). It can therefore be fixed independently of the alcohol species without affecting the quality of the fit. The physical reason for this is that the radius R_{ad} is determined by the external parameters like argon concentration (via R_0), driving pressure, etc., on which the addition of small amounts of alcohol has very little influence. Here we fixed it at $R_{\text{ad}} = 1.25$. Best fits of the parameter A_{alc} for $T_{\text{max}}(n_b = 0) = 15\,000$ K [16] are listed in Table I [25].

The small value of B shows that adiabaticity is achieved close to R_{min} , in agreement with Rayleigh-Plesset simulations [16].

The most striking result of the fit is the strong increase of A_{alc} with increasing carbon chain length. This should be expected as the longer alcohols are more hydrophobic and accumulate more strongly at the gas-water interface. For the same concentration inside the bubble, and consequently the same amount of light reduction, very different alcohol bulk concentrations are needed, as observed. We also find that the required alcohol concentration n_g inside the gas bubble for halving the intensity is always very similar, $n_g \approx 0.01\text{--}0.02$, regardless of the type of alcohol. This resembles the result in [21] for MBSL, where the light intensity is roughly independent of the kind of alcohol added if plotted against the alcohol *surface concentration* at the gas-water interface.

According to the theory presented above, the resulting light intensities are a function of both n_g and f_{alc} , so that one would not expect completely universal concentrations n_g . We observe, however, that after fixing B , the relative intensity is a unique function of the *adiabatic exponent* γ *only*. We can thus test the theory by plotting I vs γ , where all the data for the different alcohols should collapse onto one *universal curve*. Indeed, Fig. 2 reveals that the data, when plotted in this fashion, show a degree of universality even higher than the aforementioned dependence of MBSL intensity on surface concentration of alcohol (Fig. 8 of Ref. [21]). Figure 2 is also an *a posteriori* confirmation of

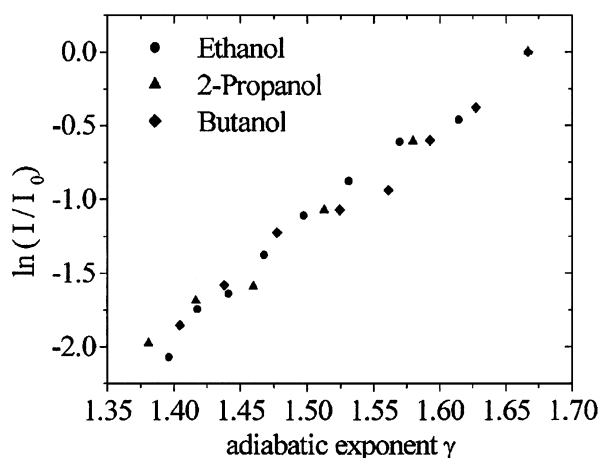


FIG. 2. Relative light intensity data as in Fig. 1, now plotted vs the effective adiabatic exponent γ of the argon-alcohol mixture. All data collapse onto one universal curve.

our assumption that the light is of essentially *thermal* origin and that it is the adiabatic heating of the argon-alcohol gas mixture which causes the emission.

We will now theoretically calculate the proportionality constants A_{alc} in Eq. (1) and thereby get further insight into the mechanism that squeezes the alcohols into the bubble. For dilute solutions the bulk concentration n_b of surfactant is related to its surface excess Γ_s and the change in surface tension σ via the Gibbs relation [26],

$$\Gamma_s = -\frac{n_b}{k_B T} \left(\frac{\partial \sigma}{\partial n_b} \right)_T. \quad (6)$$

The maximum achievable (critical) surface excess is given by close-packing of the surfactant molecules on the surface, each of which occupies an area of about 0.25 nm^2 [27], thus defining $\Gamma_{s,\text{crit}} = (0.25 \text{ nm}^2)^{-1}$. We will show below that the results of the theory do not depend on the exact area per molecule. $\Gamma_{s,\text{crit}}$ implies a critical number of alcohol molecules sitting on the interface at bubble collapse, $N_{\text{crit}}(R_{\text{min}}) = \Gamma_{s,\text{crit}} 4\pi R_{\text{min}}^2$. This number must be compared with the number of alcohol molecules which are “loaded” onto the surface at the bubble radius maximum, $N(R_{\text{max}}) = \Gamma_s 4\pi R_{\text{max}}^2$. We now assume that the alcohol molecules will not desorb or diffuse away in the short time interval of bubble collapse, but that the total excess of alcohol at bubble minimum, $\Delta N = N(R_{\text{max}}) - N_{\text{crit}}(R_{\text{min}})$, will enter the bubble, resulting in the alcohol concentration

$$n_g = \Delta N / (N_{\text{Ar}} + \Delta N) \quad (7)$$

in the gas bubble. Eventually, this alcohol will be “burned” (just as the nitrogen or oxygen molecules sucked into the bubble [8]), and the reaction products will dissolve in the water.

For the forcing pressures (≈ 1.3 atm) and argon concentrations ($\approx 0.2\%$ – 0.4% of saturation) of our experiment, a typical value for the ambient radius is $R_0 = 5 \mu\text{m}$ [3,4], corresponding to $N_{\text{Ar}} \approx 1.67 \times 10^{10}$. Minimum and maximum radii in this regime are $R_{\text{min}} \approx R_0/10$ and $R_{\text{max}} \approx 10R_0$, respectively [7]. With $\partial\sigma/\partial n_b$ from Table I we get $N_{\text{crit}}(R_{\text{min}}) \approx 1.3 \times 10^7$, whereas in the experimental range of values for n_b we have $N(R_{\text{max}}) \approx 1.3 \times 10^9$ for ethanol and $N(R_{\text{max}}) \approx 1.2 \times 10^9$ for butanol. In all cases, $N_{\text{Ar}} \gg N(R_{\text{max}}) \gg N_{\text{crit}}(R_{\text{min}})$ so that (7) simplifies to $n_g \approx N(R_{\text{max}})/N_{\text{Ar}}$. Thus, the exact value of $\Gamma_{s,\text{crit}}$ does not matter, as nearly all alcohol molecules which accumulate at the bubble surface at maximum get squeezed into the bubble at collapse.

From Eqs. (6) and (7) we obtain an *a posteriori* justification of the assumed linear relation between n_g and n_b for small $n_b < N_{\text{Ar}} \left[\frac{4\pi R_{\text{max}}^2}{k_B T} \left| \left(\frac{\partial \sigma}{\partial n_b} \right)_T \right| \right]^{-1}$. The desired theoretical value of A_{alc} is then

$$A_{\text{alc,th}} = \frac{4\pi R_{\text{max}}^2}{N_{\text{Ar}} k_B T} \left| \left(\frac{\partial \sigma}{\partial n_b} \right)_T \right|. \quad (8)$$

We find good agreement with the fitted values, see Table I. As $A_{\text{alc,th}}$ depends on R_{max} , the experiment was conducted

such that for all three alcohols a bubble with $R_0 \approx 5 \mu\text{m}$ was obtained, giving roughly the same R_{max} .

We stress that, as in MBSL [22], it is *not* the liquid vapor pressure which determines γ : it is highest for ethanol and lowest for butanol (Table I), which would suggest ethanol as the most efficient light quenching agent.

Two crucial assumptions were made in deriving (8), which have to be checked: (i) Equation (6) is an equilibrium formula; therefore, there has to be enough time for the bubble to accumulate $N(R_{\text{max}})$ alcohol molecules within, say, half a driving period. (ii) The collapse must be fast enough to ensure that the excess alcohol does not diffuse back into the liquid but jumps into the bubble.

Condition (i) implies that N_{dif} , the number of alcohol molecules that can attach to the surface within half a cycle, be greater than $N(R_{\text{max}})$. We assume a diffusion-limited adsorption process and estimate $N_{\text{dif}} \approx 4\pi R_{\text{max}}^2 l_{\text{dif}} n_b \times N_A \rho / M$, where N_A is Avogadro's constant, ρ the density of water, M its molecular mass, and $l_{\text{dif}} = (D/2f)^{1/2}$ the diffusive length scale. Thus we demand

$$r_{\text{dif}} \equiv \frac{N_{\text{dif}}}{N(R_{\text{max}})} = \left(\frac{D}{2f}\right)^{1/2} \frac{GT}{|(\partial\sigma/\partial n_b)_T|} \frac{\rho}{M} > 1, \quad (9)$$

where G is the universal gas constant. Table I shows that (9) is well fulfilled for ethanol and propanol, and is just marginally valid for butanol. The latter may account for the relatively large deviation between A_{alc} and $A_{\text{alc,th}}$ for butanol (see Table I). As surface excesses become even larger for higher alkanols, we predict deviations from this theory in experiments with, e.g., pentanol or hexanol.

To assess condition (ii) we make a worst-case estimate, disregarding the surface affinity of the alcohols, allowing them to diffuse freely during the collapse which lasts typically $\Delta t_{\text{col}} \sim 1$ ns. A typical diffusion distance is then $\sim (D\Delta t_{\text{col}})^{1/2} \sim 1$ nm, which is on the order of a molecule length, and implies that the alcohol cannot escape from the bubble surface during collapse.

For MBSL, Grieser and co-workers suggested that the alcohols and their reaction products accumulate in the bubble only over many cycles [22]. Such an accumulation might also occur in SBSL [20]. However, we believe that SBSL bubbles become too hot to sustain and accumulate nonsoluble molecules such as C_2H_2 . A crucial experiment, to distinguish between the picture of Refs. [20,22] and the present one, would be to suddenly increase the forcing pressure of a non-SL argon bubble in the alcohol-water mixture as done in [13] for air and argon bubbles in pure water: If accumulative processes over many cycles play a role, the bubble should still glow brightly for some period of time, in spite of the alcohol.

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