molecules. At $w_0 = 5$ the photoionization yield is increased because of (a) increased water interactions as indicated by the larger normalized deuterium modulation depth and (b) disorganized water at the water pool interface. At larger w_0 from $w_0 = 10$ to 30 the water organization factor is dominant and accounts for the monotonic decrease in photoionization yield.

There also appears to be an alkyl chain length effect on the photoionization yield of the alkyl carbazoles. This does not correlate with any normalized deuterium modulation depth differences and so does not reflect changes in the strength of water interactions. The most prominent alkyl chain length effect is at $w_0 = 5$ where the photoionization yields decrease in the order $CzC_4TAB > CzC_8TAB > CzC_{12}TAB$. This may be related to the orientation of the carbazole moiety with respect to the AOT/water interface. The two additional methyl-terminated alkyl chains on the carbazole framework appear to orient the carbazole less favorably for photoionization as the trimethylammonium-terminated alkyl chain length increases.

Conclusions

The photoionization efficiency of phenothiazinyl and (carbazolyl alkyl)trimethylammonium bromides in frozen solutions of AOT reverse micelles shows that the greatest degree of photoionization control is achieved by variation of $w_0 = [H_2O]/[AOT]$. Maximum photoionization is found for $w_0 = 5$ because of two contributions: (a) enhanced water interactions with the solute and (b) increased water disorganization at the interface. The enhanced water interactions can be monitored by the normalized deuterium modulation depth. At larger w_0 the photoionization yield slowly decreases. No alkyl chain length effect is seen for the phenothiazine derivatives, which is consistent with earlier studies on phenothiazine alkyl sulfonates. For the carbazoles a weak alkyl chain effect is observed, which may be related to orientation differences of the carbazyl moiety relative to the AOT/water interface.

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Registry No. PC_4TAB, 130904-78-8; $PC_{12}TAB$, 130904-79-9; CzC_4TAB, 98809-41-7; CzC_8TAB, 116054-04-7; $CzC_{12}TAB$, 116054-05-8; AOT, 577-11-7.

Sonoluminescence from Alkali-Metal Salt Solutions

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Sonoluminescence spectra from alkali-metal salt solutions in water and in primary alcohols are characterized by unusually broad resonance line emission from excited-state alkali-metal atoms. The spectral width and positions of sonoluminescence from potassium in primary alcohols are independent of both solvent vapor pressure and inert gas (Ar/He) ratio. Since the intensity of cavitational heating is dependent on both of these parameters, alkali-metal sonoluminescence cannot be used to determine the local conditions created by acoustic cavitation, contrary to earlier reports. In contrast, the intensity of this sonoluminescence is highly dependent on these two factors. This apparent paradox is explained if the excited-state alkali-metal atoms are the result of secondary reactions of metal ions with high-energy radicals formed directly in the cavitation event. The large line width is caused by rapid collisional deactivation of the excited-state atoms.

Introduction

The chemical effects of ultrasound in homogeneous systems are caused by acoustic cavitation: the formation, growth, and implosive compression of bubbles in solution.[1] The violent collapse of these bubbles heats the gas and vapor in these bubbles rapidly, causing their contents to react. The conditions present during cavitational collapse remain to be fully characterized. Sonoluminescence is associated with acoustic cavitation and can provide a spectroscopic probe of the species and conditions produced during cavitation.[2] This work began as an attempt to extend a study of sonoluminescence from aqueous alkali-metal salt solutions by Sehgal et al.;[3] the present results, however, challenge their conclusions.

Sonoluminescence from an alkali-metal salt solution was first reported by Lewschin and Rschevkin[4] in 1937. Gunther and co-workers[5] reported sonoluminescence from aqueous LiCl and NaCl solutions under Ar, and Heim[6] reported that the sonoluminescence spectrum of NaCl in water was asymmetric and broadened. Taylor and Jarman[7] made a similar observation for NaCl solutions irradiated at 16 and 500 kHz under both Kr and Xe. Sehgal et al. published[3] high-resolution sonoluminescence spectra from aqueous KI and NaI solutions that were significantly broadened and slightly shifted compared to low-pressure, gas-phase emission. They assumed that the broadening and shifting were due to the high temperature and pressure of cavitational collapse, and they used the magnitude of the broadening and shifting to calculate apparent temperatures and pressures.

The initial aim in this work was to use sonoluminescence from alkali-metal salt solutions as a probe of acoustic cavitation. The intention was to explore the effects of various extrinsic parameters

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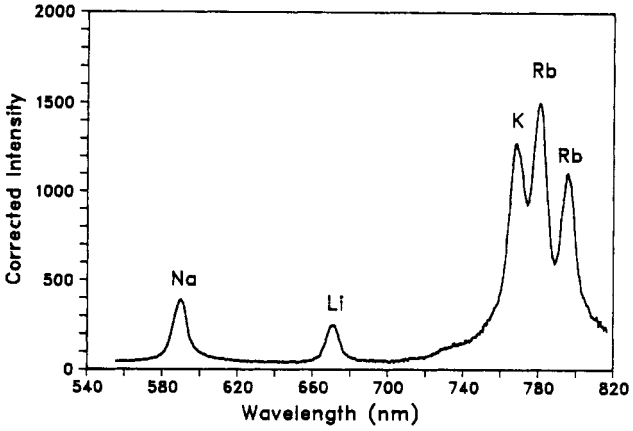

Figure 1. Low-resolution sonoluminescence spectrum of the alkali metals. Emission shown is from a 0.1 M Li^+, 0.05 M Na^+, 0.05 M K^+, 0.05 M Rb^+ (as the 1-$OC_8H_{17}^-$ salts) in 1-octanol under Ar. Average of 10 100-s spectra.

on the temperatures and pressures reached during cavitation. It was found, however, that the line width and shift of the alkali-metal sonoluminescence are independent of extrinsic parameters known to affect the temperature of cavitational collapse (e.g., solvent vapor pressure, inert gas thermal conductivity), indicating that this emission does not originate directly from the cavitational hot spot. Alkali-metal sonoluminescence therefore *cannot* be used to calculate cavitational temperatures and pressures.

Experimental Section

Sonoluminescence spectra were collected with instrumentation described in detail elsewhere.[2] High-intensity ultrasound was generated by a titanium immersion horn (Heat Systems Ultrasonics Model 375W) operating at 20 kHz and ≈60 W/cm^2. The stainless steel cell with gas ports, cooling jacket, and quartz window has also been described elsewhere.[8] The sonoluminescence was dispersed with a Thermo Jarrell-Ash MonoSpec-18 0.25-m spectrograph. Low-resolution spectra were collected with a 300 groove/mm grating blazed at 300 nm with a 150-μm entrance slit, and higher resolution spectra were collected with a 1200 groove/mm grating blazed at 500 nm with a 50-μm entrance slit. The detector was a Princeton Instruments IRY-512N intensified diode array detector controlled by a ST120 optical multichannel analyzer. Mercury, neon, and krypton low-pressure lamps were used for wavelength calibration. The relative response functions for the low-resolution spectrum were determined with a 360-W tungsten lamp that had been calibrated against a 1000-W tungsten secondary standard lamp from the Eppley Laboratory.

Solutions of the alkoxide salts of the alkali metals were prepared by addition of the appropriate 1-alcohol (Aldrich, 99% pure or better) to the metal (Aldrich, 99.9% pure or better) under inert atmosphere. Solvents used in the vapor pressure study were 1-octanol, 1-heptanol, 1-hexanol, 1-pentanol, 1-butanol, 1-propanol, and water. The reaction mixture was heated or cooled to control the rate of reaction. Potassium was chosen for the medium-resolution studies because its D line splitting is greater than for Na and Li, while its expense and hazard are less than Rb.

Argon was purified with an activated copper-on-alumina catalyst (BTS from BASF) immediately before use. Gases were mixed prior to sparging of solutions. For 30 min prior to ultrasonic irradiation, solutions were sparged at 0.5 ± 0.1 scfh through a 20-gauge Teflon tube at the cell bottom (≈2 cm from horn tip); the gas flow was continued as spectra were collected.

Vapor pressures were calculated from the Antoine equation

$$\log V_p = A - B/(t + C)$$

where V_p is the vapor pressure, t is the temperature in °C, and

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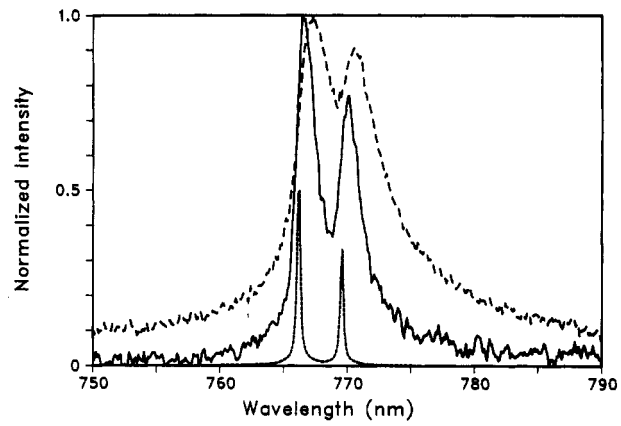

Figure 2. Normalized medium-resolution potassium emission. Intensities have been normalized relative to the most intense peak. Slit width and source position for all spectra are the same. (---) Sonoluminescence from 0.50 M KOC_8H_{17} in 1-octanol, average of 10 100-s spectra. (—) Spectrum from 2.0 M KOH in water, average of 20 100-s spectra. (···) Emission from K hollow cathode lamp; spectrum intensity has been divided by 2 for clarity.

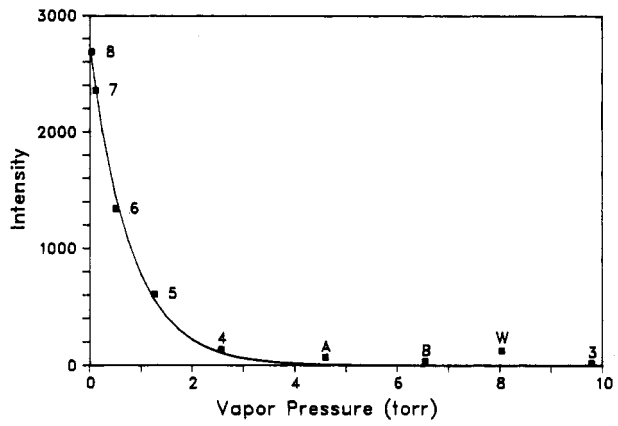

Figure 3. Vapor pressure dependence of potassium sonoluminescence from 1-alcohols and water under argon. Numbers indicate numbers of carbons in each alcohol: A = 80/20 v/v 1-butanol/1-propanol; B = 50/50 v/v 1-butanol/1-propanol. Solid line is a fit to the equation $I_{SL} = be^{-cP}$, where b and c are constants and P is the system vapor pressure.

A, B, and C are empirical constants for each liquid.[9] Raoult's law behavior was assumed for calculating the vapor pressure of solutions containing two alcohols. The temperature of the reaction cell was measured with a copper–constantan thermocouple.

Results and Discussion

The sonoluminescence spectrum from a 1-octanol solution of Li^+, Na^+, K^+, and Rb^+ (as the 1-octyl alkoxide salts) is shown in Figure 1. This spectrum is similar to those of Sehgal et al. for the sonoluminescence of sodium and potassium salts in water,[3] i.e., the emissions are at the expected wavelengths and are significantly broadened. This is the first report of Rb sonoluminescence, probably due to the sparing solubility of Rb salts in water and the poor sensitivity of photomultipliers in this region.

To test the assumption of Sehgal et al. that the position and line width of alkali-metal sonoluminescence reflect the temperature and pressure of the cavitation event,[3] two sets of experiments were run to determine the influence on the sonoluminescence spectra of parameters known to vary the cavitational temperature. The sonoluminescence intensities, peak positions, and line widths were examined as a function, first, of the solvent vapor pressure and, second, of the thermal conductivity of dissolved gas.

Effect of Vapor Pressure on Sonoluminescence. The influence of solvent vapor pressure on potassium sonoluminescence is shown

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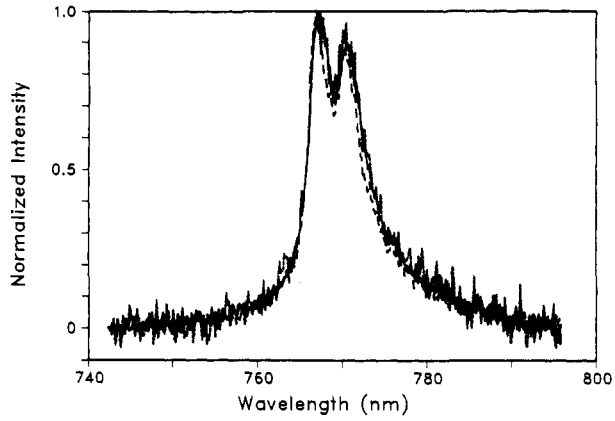

Figure 4. Normalized sonoluminescence spectra vs vapor pressure, from 0.50 M K^+ as the alkoxide salts in alcohol solutions. Baselines have been subtracted from each spectrum. Intensities have been normalized relative to the most intense peak. (—) Spectrum from 0.50 M KOC_8H_{17} in 1-octanol, vapor pressure 0.054 Torr. Average of 10 100-s spectra. (- - -) Spectrum from 0.50 M KOC_5H_{11} in 1-pentanol, vapor pressure 0.82 Torr. Average of 10 100-s spectra. (···) Spectrum from 0.50 M K^+ in 25/75 v/v 1-butanol/1-octanol, vapor pressure 0.95 Torr. Average of 20 100-s spectra from two sets of experiments.

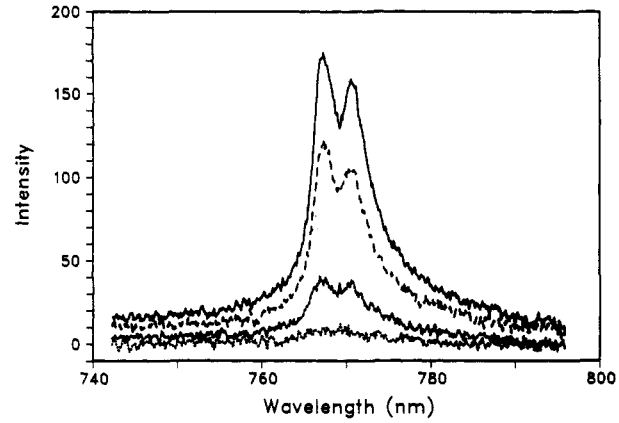

Figure 5. Potassium atom sonoluminescence from 1-octanol under Ar/He mixtures: (—) pure argon; (- - -) 1/1 argon/helium; (- · -) 1/4 argon/helium; (···) pure helium. All are the average of 10 100-s spectra.

in Figures 3 and 4. The total intensity of the sonoluminescence emission decreases exponentially with increasing vapor pressure, as can be seen in Figure 3. This is the behavior both expected and observed for homogeneous sonochemical reactions.[10]

The temperature reached in a cavitational bubble upon collapse, T_{max}, can be estimated for a noncondensable gas with eq 1, where

$$T_{max} \approx T_0 P_a(\gamma - 1)/Q \quad (1)$$

T_0 is the initial temperature, P_a is the acoustic pressure, γ is the ratio of the heat capacities (C_p/C_v), and Q is the gas pressure in the bubble before collapse.[1d] Q can be approximated as the sum of the gas and vapor pressures in the bubble immediately before collapse. As the vapor pressure of the system is increased, the peak temperatures reached during cavitation decrease for three reasons. First, increased vapor pressure increases Q in eq 1. Second, increased solvent vapor in the bubble decreases γ; the value of γ for Ar is 1.66 at all temperatures, while for most polyatomic molecules $\gamma \approx 1.2$ at room temperature and decreases as the temperature increases. Finally, the condensation of the vapor during cavitational compression also decreases the maximum temperature reached.

For chemical reactions showing Arrhenius temperature behavior, we can predict a general form for sonoluminescence intensity as a function of solvent vapor pressure. Equation 2, derived

$$I_{SL} = B \exp[-CV_p] \quad (2)$$

from eq 1 and the Arrhenius equation, relates the intensity of the sonoluminescence (I_{SL}) to the vapor pressure of the system (V_p). The empirical fit to this equation is also shown in Figure 3. The exponential behavior of this data indicates that alkali-metal sonoluminescence is caused by processes occurring in the cavitational hot spot.

Contrary to expectations, however, the line width and peak position of these lines do *not* change as a function of the vapor pressure, as can be seen in the normalized potassium sonoluminescence spectra in Figure 4. The relevant line broadening mechanisms are highly temperature and pressure dependent.[11,12]

Thus, the observed line width and peak position are *independent* of cavitational conditions. The conclusion, therefore, is that the excited-state atoms are not in the hot spot of the cavitation event when the emission occurs.

The unusual width and shift of these atomic emission lines are illustrated in Figure 2, where the potassium sonoluminescence spectrum is compared to the emission spectrum of a K hollow cathode lamp. This figure shows that potassium sonoluminescence in both 1-octanol and water is very broad and that the broadening is greater in 1-octanol than in water. The hollow cathode lamp spectrum confirms that our instrumental resolution (0.17 nm, in this configuration) is much better than the observed sonoluminescence line widths (typically ≈4.5 nm in alcohol solutions).

There are three sources of spectral line broadening beyond the minimum line width determined by the natural lifetime: Doppler broadening, field broadening, and pressure broadening.[12] Pressure broadening is most likely the source of the width of the sonoluminescence lines. Pressure broadening is caused by collisional deactivation and is a consequence of the Heisenberg uncertainty principle. Doppler broadening can be eliminated because the line widths are independent of factors that change the cavitational temperature (i.e., vapor pressure and gas thermal conductivity). Field broadening is an unlikely source of the increased line width since cavitational effects are primarily thermal in origin.[1]

For pressure broadening, the lifetime of the excited state can be calculated from the line width, and the spectra in Figure 2 indicate that the collision lifetime is ≈0.05 ps. For comparison, the natural lifetimes of the excited states that make up the doublet at 11.4 and 6.3 ns,[13] and the collisional lifetime of a K atom in a 2600 K, 1 bar flame is calculated to be 0.4 ns.[12]

The lifetime of the excited state can be used to estimate the density of the environment of the emitting species.[12] Equation 10 relates the density (N) to the lifetime (τ), the collision cross

$$N^{-1} = 2\tau\sigma_{12}^2[2\pi RT(m_1 + m_2)/m_1m_2]^{1/2} \quad (10)$$

section (σ_{12}), the masses (m_1, m_2) of the emitter and quencher, and the temperature (T). The density calculated with this equation are roughly in the range of condensed phases. For example, if we assume a collision cross section with dodecane of ≈100 Å^2, then at 2000 K, N is very roughly 1.5 g/cm^3.

Effect of Gas Thermal Conductivity on Sonoluminescence. The temperature of the cavitational event was varied in a second manner by changing the sparge gas from Ar to He. These gases are both chemically inert, but He has a thermally conductivity 9 times greater than Ar. Upon cavitational collapse a helium-filled bubble will be colder than an argon-filled one. The same total heat is generated during compression, but it is conducted away more rapidly by He than Ar. Figure 5 shows sonoluminescence

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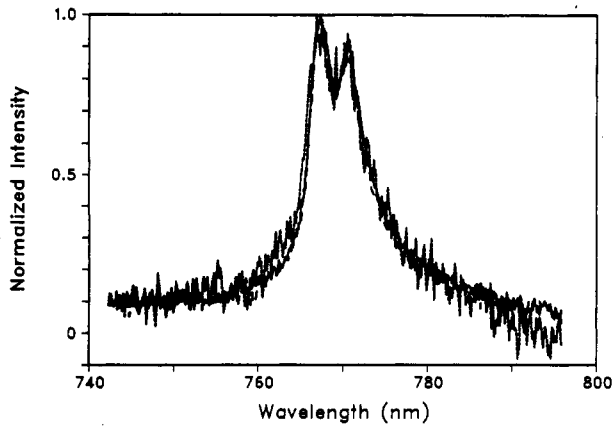

Figure 6. Normalized potassium atom sonoluminescence from 1-octanol under Ar/He mixtures. All are the average of 10 100-s spectra: (—) pure argon; (---) 1/1 argon/helium; (- - -) 1/4 argon helium. Intensities have been normalized relative to the most intense peak.

spectra from K^+ in 1-octanol under a range of Ar/He mixtures. As expected, the sonoluminescence intensity decreases as the fraction of He is increased. The line width and peak position, however, are *unchanged*, as shown in the normalized spectra in Figure 6. This demonstrates again that the line width and peak position are independent of cavitational temperature.

The peak positions also confirm that the excited-state potassium atom is not in the gas phase at the time of emission. The resonance lines of the alkali metals are red-shifted in the gas phase by high pressure of Ar but are *blue-shifted* by high pressures of He.[11] An Ar pressure of 50 bar shifts the potassium peaks about 1.2 nm to the red, while 50 bar He induces a 0.3-nm blue shift. Pressures developed during cavitation are in the hundreds of bar.[1] Differences of this magnitude would have been easily resolved with our spectrometer. Figure 2 shows, however, that potassium sonoluminescence from 1-octanol solutions under Ar is red-shifted compared to emission from the hollow cathode lamp, and Figures 5 and 6 show that the red shift is the same when Ar or He is sparged through the solution.

Mechanism of Alkali-Metal Sonoluminescence. The mechanism of sonoluminescence from alkali-metal salt solutions must take into account two seemingly contradictory observations. First, the line width and peak position of the emission do not change as a function of cavitation temperature: they are unaffected by changes in the solvent vapor pressure (Figure 4) or gas composition (Figure 6). Second, however, the intensity of the sonoluminescence does decrease with decreased cavitational temperature (Figures 3 and 5), as expected for homogeneous sonochemical reactions.

Equations 3–9 present a chemical mechanism that is consistent with our observations. Each step of this scheme is well precedented in the literature. Radicals are produced from the ultrasonic irradiation of water,[14] alkanes,[10] halocarbons,[15] and nonaqueous liquids in general;[10] they are also the source of excited-state CO_2 that was assigned[2] as the emitting species in the sonoluminescence from 1-octanol. The species formed from ultrasonic irradiation of water[14] are shown in eq 3. High-energy species from the ultrasonic irradiation of primary alcohols will also include carbon-based radicals (as are seen from the alkane sonolysis)[10] and oxygen based radicals[16] such as RO• and atoms, as shown in eq 4. These radicals (denoted P• and Q•) are formed in the hot spot of the cavitation event. They diffuse rapidly out into solution, where they react with the alkali-metal atoms.

$$H_2O \xrightarrow{)))} H^\bullet + HO^\bullet \quad (3)$$

$$ROH \xrightarrow{)))} H^\bullet + HO^\bullet + R^\bullet + RO^\bullet + O \quad (4)$$

$$P^\bullet + M^+ \rightarrow M + P^+ \quad (5)$$

$$P^\bullet + Q^\bullet + M \rightarrow M^* + PQ \quad (6)$$

$$P^\bullet + MOH \rightarrow M^* + ROH \quad (7)$$

$$M^* \rightarrow M + h\nu \quad (8)$$

$$M^* + S \rightarrow M + S + \text{heat} \quad (9)$$

In the gas phase, such radicals are capable of both reducing alkali-metal ions to atoms (eq 5) and of promoting the atoms to the excited state via chemiluminescence[17a] (eq 6). These reactions may actually proceed in several steps through discrete intermediates. Reaction 5 is known[17a] to occur in the gas phase in flames for [P•,Q•] equal to [H,H], [H,OH], [CO,O], and [O,O]. Reaction 5 with P• = Q• = H was proposed[7] by Taylor and Jarman for sonoluminescence from NaCl in water. Another possibility is that the cation is reduced and excited in one step (eq 7), as has also been reported in flames.[17b] Once the alkali-metal atom is in the excited state, it can then either emit a photon (eq 8) or be quenched by a solvent molecule (S in eq 9). It is the rapid quenching of the excited state (eq 9) that leads to the large line width of the resonance lines.

More evidence for chemical excitation is the observation of the small shoulder to the high-energy side of the K resonance line, around 740 nm in Figure 1. This has been assigned[3,17] to emission from a metal complex (K–X, where the identity of X is unknown) and is seen in very high temperature flames where considerable chemical excitation is occurring.

The proposed mechanism is consistent with the observed effects of experimental parameters. The high-energy radicals produced from solvent vapor in the cavitation event then diffuse out of the hot spot where they react with alkali-metal ions to produce excited-state atoms. This explains the sonoluminescence from nonvolatile ions, which would not have been expected inside the cavitating bubble. A small fraction of the excited metal atoms emit, while the remainder are rapidly quenched by collisions with solvent molecules. The line width of the resonance lines do not change as cavitation conditions change because the environment around the emitting atom is not in the cavitation hot spot, but rather out in the surrounding solution. The effective concentration of the solvent (S in eq 9) in this second reaction zone, and thus the rate of quenching and the lifetime of the excited state, is essentially independent of solvent, solvent vapor pressure, or gas thermal conductivity. This leads to the similarity of the normalized spectra shown in Figures 4 and 6.

The existence of this second reaction zone has already been well documented. The rapid compression of the cavitation bubble forms a hot spot out of the initially gas-phase bubble. This then also heats an initially liquid shell around the collapsed bubble, generating a superheated fluid with a liquidlike density.[19] The temperatures of these two reaction zones have been determined by comparative rate thermometry[19] to be about 5200 K for the initially gas-phase zone and about 1800 K for the initially liquid zone in alkanes with a vapor pressure of 5 Torr under Ar. Radical quenching[20] and spin-trapping[21] experiments have provided cor-

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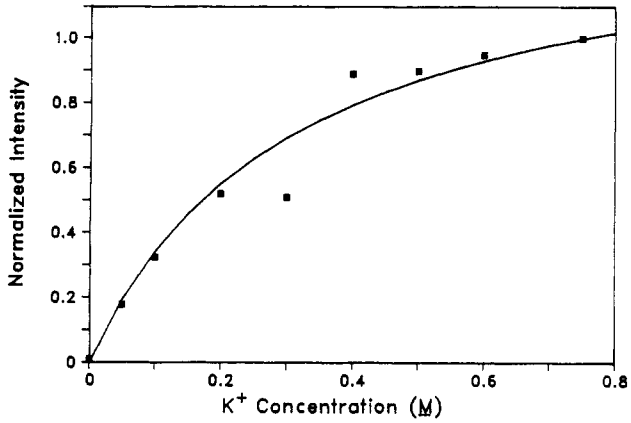

Figure 7. Potassium ion concentration dependence of sonoluminescence from KOC_8H_{17} solutions in 1-octanol: (■) experimental data; (—) fit to steady-state kinetic expression, $I_{SL} = d[M^+]/(e + f[M^+])$.

roborating evidence for this two-site model and the diffusion of radicals from the hot spot to the heated shell and bulk liquid.

The proposed mechanistic scheme also explains the decrease in sonoluminescence intensity with decreasing cavitational temperature (i.e., increased solvent vapor pressure or sparge gas thermal conductivity). The rate of production of radicals (eq 4) decreases with decreased cavitational temperature, which decreases the rate of the subsequent reduction and chemiluminescent reactions (eqs 5 and 6). In addition, the volume of the surrounding heated fluid (and thus the number of alkali-metal atoms involved) also decreases as the temperature of the cavitation event decreases.

Further evidence consistent with our mechanism is found with the sonoluminescence intensity as a function of K^+ concentration, shown in Figure 7. The observed saturation kinetics[22] are a consequence of the secondary nature of the reactions that generate M*. The primary process is the formation of radicals by the high temperatures of the cavitation event. At low alkali-metal ion concentrations, the rate of the activation reactions (eqs 5–7) is slow compared to the rate of other radical-trapping reactions. At high alkali-metal ion concentrations, the rate of the activation reactions dominate, and all sonochemically generated radicals are trapped by alkali-metal species. The change in the relative rates of these reactions leads to the observed saturation kinetics. The usual steady-state kinetics analysis yields eq 11, where d, e, and f are constants involving many separate reaction rate coefficients. The solid line in Figure 7 is the best fit to eq 11. Given the large number of participating reactions, further analysis of the relative values of these constants is not justified.

$$I_{SL} = d[M^+]/(e + f[M^+]) \quad (11)$$

The line width from potassium sonoluminescence in water is narrower than that from 1-octanol (Figure 2). The width of the resonance line is a direct function of the lifetime of the excited state, which in turn in inversely related to the rate of the quenching reaction, eq 9. This reaction involves the conversion of electronic energy of the alkali-metal atom to vibrational energy of the solvent molecule. The triatomic water is less effective than the polyatomic 1-alcohols in this, giving a longer excited-state lifetime and a narrower sonoluminescence line width, as observed.

Conclusions

The major consequence of this study is that the use by Sehgal et al.[3] of high-resolution sonoluminescence spectra of Na and K emission to calculate the temperature of the cavitation event is incorrect. The line widths and peak positions of these spectra are insensitive to experimental parameters that affect cavitational heating, such as total vapor pressure and the thermal conductivity of the sparge gas. Thus, alkali-metal sonoluminescence is *not* a valid probe of the conditions produced during acoustic cavitation. The considerable line broadening observed in these systems is ascribed to pressure broadening. As calculated from the line width of the resonance lines, the lifetime of the potassium excited state is unusually short, ≈0.05 ps. The source of the unusual line width is from collisional deactivation from solvent molecules in the rapidly heated fluid immediately surrounding the collapsing bubble. Radicals formed during the cavitation event are responsible for the formation of the excited-state alkali-metal atoms.

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Registry No. Ar, 7440-37-1; He, 7440-59-7; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8.

(21) (a) Kondo, T.; Krishna, C. M.; Riesz, P. *Int. J. Radiat. Biol.* **1988**, *53*, 891. (b) Kondo, T.; Krishna, C. M.; Riesz, P. *Radiat. Res.* **1988**, 116, 56.

(22) In principle, this behavior could also arise from self-absorption. Self-absorption occurs in gas-phase atomic emission spectroscopy at high atomic concentrations and can be recognized by a decrease in the intensity in the center of an emission line. It can be ruled out in this case for three reasons: the emission lines are very broad, the emission lines do not change shape as the concentration is increased, and the atomic concentration of potassium atoms is very low.

Infrared Spectroscopic Studies of Concentrated Aqueous Electrolyte Solutions

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Infrared spectra of the OD stretching vibration of isotopically dilute HDO molecules in aqueous solutions of $Ni(ClO_4)_2$ and $Mg(ClO_4)_2$ are presented. For all concentrations, the spectra comprise four components; those corresponding to HDO molecules interacting with the anion, in the cation coordination sphere, in solvent-shared ion pairs, and in the bulk. Band parameters are given for these bands, as are quantitative estimates of the distribution of these species at all concentrations.

Introduction

The stretching vibrations of the water molecule are, in principle, ideally suited as probes of ionic hydration in aqueous solutions. These vibrations are highly sensitive to the extent of hydrogen bonding and thus to the local environment in the solution; also, the time scale of these vibrations makes possible the detection of species with lifetimes as short as 10^{-13} s, which is shorter than most rearrangement processes occurring in solutions. However, the stretching vibration bands of liquid H_2O are extremely broad

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