

Review

Sonochemistry and sonoluminescence in ionic liquids, molten salts, and concentrated electrolyte solutions

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Abstract

Ionic liquids have favorable intrinsic properties that make them of interest as solvents for various chemical reactions. The same properties that make the liquids effective solvents also make them interesting liquids for studies involving sonochemistry, acoustic cavitation, and sonoluminescence. Recent interest in using ultrasound to accelerate chemical reactions conducted in ionic liquids necessitates an understanding of the effects of acoustic cavitation on these solvents. Here, we review our previous results on the effects of cavitation on some room-temperature ionic liquids, including the sonoluminescence spectra of molten salt eutectics and concentrated aqueous electrolyte solutions. In all cases, regardless of the essentially nonexistent vapor pressure of the solution atomic and small molecule emitters are observed in the spectra which arise from sonolysis of the ionic liquids.

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Contents

1. Introduction	3513
2. Sonochemistry and sonoluminescence of room-temperature ionic liquids.	3515
3. Effects of ultrasonic irradiation on molten salt eutectics	3515
4. Single-bubble acoustic cavitation in concentrated aqueous electrolyte solutions	3516
5. Conclusions.	3516
Acknowledgments	3517
References	3517

1. Introduction

Ionic liquids are finding widespread use as solvents in a variety of applications, including biphasic catalysis, liquid–liquid extraction, and organometallic synthesis [1–3]. Recent research has focused on air-stable, room-

temperature ionic liquids composed of asymmetric *N,N'*-dialkylimidazolium cations with a variety of bulky anions such as PF_6^- , BF_4^- , and BPh_4^- . These ionic liquids are attractive because of their unique intrinsic properties, such as high thermal stability, large liquid range, and negligible vapor pressure [4]. The uses of ionic liquids as the media for synthetic and catalytic studies are varied and numerous [5], including the synthesis and use of transition–metal nanoparticles as recyclable

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catalysts [6,7]. While the majority of work on room-temperature ionic liquids has focused on using the solvents as reaction media, recent research has demonstrated that organometallic catalysts and compounds can be incorporated directly into one of the ionic moieties [8–11]. For example, Audic et al. [9] synthesized an alkyl imidazolium salt-supported ruthenium catalyst for ring-closing olefin metathesis, and Gao et al. [10] reported the first synthesis of room-temperature ionic liquids with ferrocenylmethyl-substituted cations. It is apparent from the wide-ranging applications that the unique properties of ionic liquids make them suitable for many chemical and physical studies. It is precisely these unique properties that make ionic liquids particularly interesting for use in sonochemical reactions.

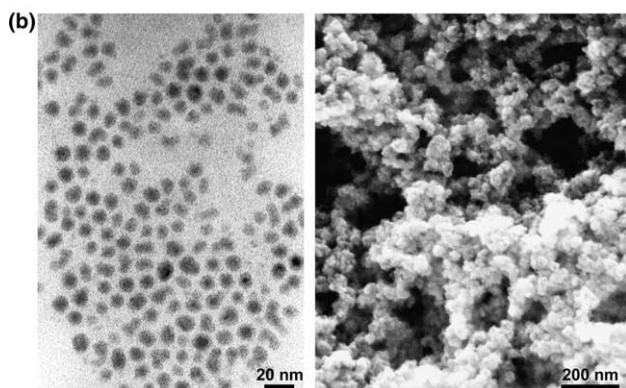
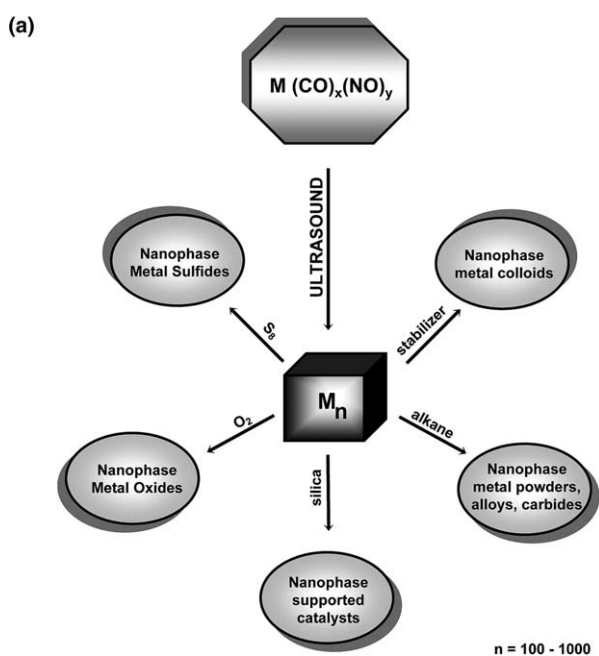


Fig. 1. Organometallic sonochemistry has important and diverse applications. (a) Schematic representation of the range of materials prepared by the sonolysis of organometallics [17,18]. (b) TEM of amorphous nanocolloid of Fe prepared by the sonolysis of $\text{Fe}(\text{CO})_5$ under Ar with oleic acid to trap the nanoparticles (left) and SEM of agglomerated nanostructured iron prepared from the sonolysis of $\text{Fe}(\text{CO})_5$ under Ar without a surface trapping agent.

Sonochemistry and sonoluminescence (SL) are a result of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid [12,13]. The rapid collapse of such bubbles results in the formation of hot spots with observed temperatures of ~ 5000 K, pressures of ~ 300 atm, and cooling rates in excess of 10^{10} K/s [14–16]. The extreme conditions generated inside cavitating bubbles are responsible for a variety of chemical and physical effects. For example, volatile organometallic precursors (e.g., $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_6$) are able to enter the vapor phase inside cavitating bubbles and after sonolysis, can produce a variety of nanostructured materials with unique morphologies and catalytic activities (Fig. 1) [17,18].

The chemical and physical effects of cavitation are highly dependent upon the contents of the collapsing bubble. The choice of solvent for sonochemical reactions is, therefore, critical. To minimize the participation of the solvent during the reactions and to maximize the temperatures and pressures reached within cavitating bubbles, low vapor pressure hydrocarbon solvents have generally been employed [19,20]. Using these solvents for sonochemistry, however, is not without some drawbacks. Significant carbon contamination of the desired nanostructured materials occurs due to sonolysis of the solvent. In addition, an upper limit is placed on the bulk temperatures at which sonochemical reactions can be effectively run, because the increased temperature increases the solvent vapor pressure, which arrests the bubble collapse [21]. Since ionic liquids have essentially no vapor pressure, they should be ideal as solvents for sonochemical reactions.

Recently, the ultrasonic acceleration of various chemical reactions has indeed been studied using ionic liquids as the solvent. Some of these reactions include the synthesis of methanofullerene derivatives [22], the *para*-selective nitration of phenols [23], and Suzuki and Heck cross-couplings [24,25]. There have also been recent reports on the sonochemical preparation of ionic liquids with 1-alkyl-3-methylimidazolium cations and various anions (e.g., halides, BF_4^- , and CF_3SO_3^-) [26,27]. Despite numerous reports of using ultrasound to accelerate chemical reactions, synthesis of organometallic and solid state species in room-temperature ionic liquids under ultrasonic irradiation are, however, surprisingly scarce. In a recent synthesis of $[(1\text{-methylimidazole})_6\text{Fe}^{\text{II}}](\text{PF}_6)_2$ using ultrasound, Jacob et al. [28] reported incorporation of the ionic liquid anion into the final product. This result underlines the importance of understanding the effects of acoustic cavitation on these ionic liquids themselves, as well as on related molten salts and concentrated electrolyte solutions. Here, we will review the sonochemistry and sonoluminescence of some room-temperature ionic liquids previously reported by our group. We will also report on SL properties of the molten salt eutectic $\text{ZnCl}_2/\text{NaCl}/\text{KCl}$, as well as those of concentrated aqueous H_2SO_4 solutions.

2. Sonochemistry and sonoluminescence of room-temperature ionic liquids

Our group has previously examined the effects of acoustic cavitation on a number of room-temperature ionic liquids including butylmethylimidazolium chloride (BuMeImCl), butylmethylimidazolium tetrafluoroborate (BuMeImBF₄), butylmethylimidazolium hexafluorophosphate (BuMeImPF₆), urea ammonium nitrate (UAN), and decylmethylimidazolium tetrphenylborate (DecMeImBPh₄) [29]. It was observed that sonication led to varying degrees of decomposition of all the ionic liquids studied. Gas chromatography–mass spectrometry (GC–MS) analysis of the headgas over each sonicated imidazolium ionic liquid indeed confirmed that decomposition was significant, forming various alkyl halides and imidazole decomposition products. Analysis of the headgas during sonication of UAN revealed the presence of NH₃ and CO₂. Note that in the absence of ultrasound, no decomposition products were detected during heating of the ionic liquids even at >150 °C.

Further evidence of the sonochemical decomposition of the ionic liquids was observed in the multibubble sonoluminescence (MBSL) spectra. During sonication of BuMeImCl and UAN, light was emitted from clouds of cavitating bubbles; this phenomenon has been observed and studied with other systems to determine the temperature and contents of the cavitating bubbles [14,15,30]. The MBSL spectra of BuMeImCl contained molecular emission from excited states of C₂ and CH (Fig. 2(a)) while the spectra from UAN were dominated by CN emission (Fig. 2(b)). Combined with ¹H NMR data and the previously mentioned GC–MS results, the MBSL spectra indicated that not only were the ionic liquids decomposing upon sonication, but the primary sonolysis products of the ionic liquids (which are volatile and therefore easily susceptible to sonochemistry themselves) were being further decomposed. Though the negligible vapor pressures of ionic liquids would intuitively lead one to predict that they would not be susceptible to sonochemical degradation, the data clearly indicates otherwise. These observations are consistent with the

two-site model of sonochemical reactions: the first site is the bubble's interior gas-phase, while the second is an initially liquid phase [31]. The initially liquid phase corresponds to either the heating of a liquid shell near the gas–liquid bubble interface or to the injection of liquid droplets by surface waves and bubble translational motion into the bubble interior followed by subsequent heating of the droplets upon bubble collapse (Fig. 3). The temperature of the heated liquid shell or droplets is thought to be ~1900 K; this temperature is much above the temperatures necessary to decompose the ionic liquids studied.

3. Effects of ultrasonic irradiation on molten salt eutectics

To limit the formation of organic decomposition products from sonolysis, our group has also explored molten inorganic salt eutectics for use in studies of acoustic cavitation. Molten salt eutectics, as with room-temperature ionic liquids, have essentially no vapor pressure in addition to lower melting points than the individual components comprising the eutectic. For example, the eutectic ZnCl₂/NaCl/KCl melts at 475 K, whereas pure NaCl melts at 1074 K thus making the salt eutectic experimentally more accessible than the pure molten salts. Molten salt eutectics also have distinct advantages over room-temperature ionic liquids in sonochemical and SL studies; molten salt eutectics are optically transparent in the spectral region of interest and will not suffer from the build-up of small carbonaceous molecules inside the bubble. Importantly, the absence of carbon-containing solvent molecules eliminates the possibility of carbon contamination of the sonolysis products.

Initial studies have focused on the 60/20/20 percent by weight ZnCl₂/NaCl/KCl molten salt eutectic which, as mentioned, melts into a relatively transparent liquid at 475 K. Analysis of the MBSL spectrum (Fig. 4) indicates a broad continuum with an unresolved Na atom emission peak from the ³S_{1/2} ← ³P_{3/2} and ³S_{1/2} ← ³P_{1/2} manifolds. With theoretically no vapor pressure, the

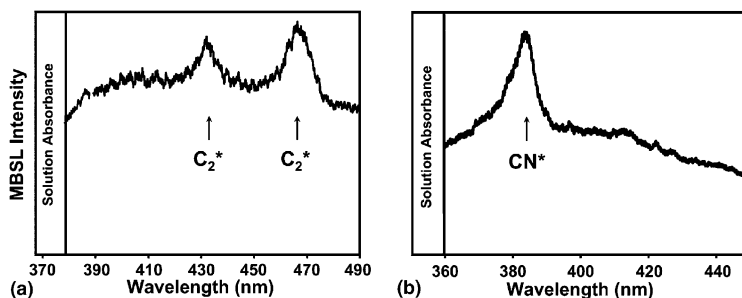


Fig. 2. MBSL spectra of: (a) BuMeImCl and (b) UAN. In both cases, the liquids begin to absorb strongly at 360 nm prohibiting spectral analysis below this wavelength. The BuMeImCl MBSL spectrum is dominated by C₂ emission while the UAN spectrum is dominated by CN emission.

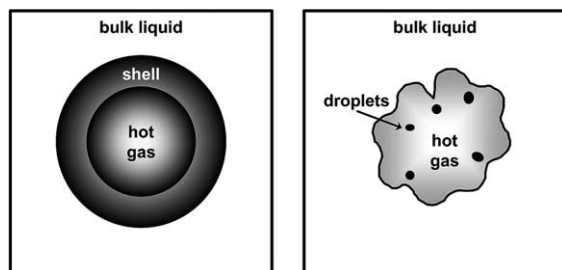


Fig. 3. Two-site model of sonochemical reactivity.

origin of the Na emission again suggests a two-site model of sonochemical reactivity. Nonetheless, inorganic eutectic salt solutions do provide an interesting avenue of research since there are no organic decomposition products. Future studies could include probing CrCl₂/LiCl/KCl eutectic in an attempt to observe Cr atom emission; the relative intensity of Cr atom emission lines would provide a spectroscopic emission temperature and thus a comparison to cavitation in hydrocarbon liquids [15].

4. Single-bubble acoustic cavitation in concentrated aqueous electrolyte solutions

A single bubble can be trapped and made to oscillate at the velocity node of a liquid-filled resonator by application of a standing acoustic wave [32]. Under certain conditions, subnanosecond flashes of light are emitted at the point of minimum bubble collapse upon each and every oscillation (single-bubble sonoluminescence, SBSL) [33]. This system is ideal for quantifying the physical conditions and identifying the chemical species generated inside the bubble during cavitation since there is no interference from other bubbles or from the container walls [34]. Though water has been the liquid of choice for studying SBSL, the spectra are typically devoid of any atomic or molecular emission that could be used to determine conditions during the bubble collapse [35]. SBSL spectra, therefore, are much different than MBSL spectra which are relatively rich in information [36]. Because of this, we have explored other less

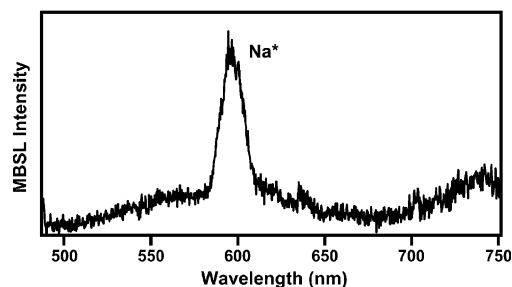


Fig. 4. MBSL spectra of 60/20/20 percent by weight ZnCl₂/NaCl/KCl molten salt eutectic. The prominent feature centered at 590 nm is due to Na atom emission.

volatile liquids for generating and studying SBSL, including polar aprotic organic liquids [37] and concentrated aqueous electrolyte solutions [38]. Similar to room-temperature ionic liquids and molten salts, concentrated aqueous electrolyte solutions have favorable properties for generating and studying sonochemistry and SL, including very low vapor pressures and moderate viscosities. Furthermore, the sonolysis products of the polar aprotic and electrolyte solutions are soluble in the bulk liquid; this is important because sonolysis products otherwise accumulate in the bubble and suppress maximum heating during bubble collapse [39].

Recently, we discovered that concentrated aqueous H₂SO₄ gives extremely intense SBSL with very informative spectra (Fig. 5) [38]. This is likely due to a combination of the very low vapor pressure (30 mTorr at 295 K) and increased viscosity (25 cP) of the concentrated H₂SO₄ solution relative to pure water. Even at these low vapor pressures, however, there is still evidence of sonolysis of solution vapor in the SBSL spectra just as is observed in the MBSL spectra of room-temperature ionic liquids and molten salt eutectics. For example, when 85% H₂SO₄ contains a low concentration of dissolved helium (whose large thermal conductivity lowers the temperatures formed during cavitation), emission from SO₂ and SO are observed in the SBSL spectra (Fig. 6). The SO₂ and SO likely arise from decomposition of vaporous H₂SO₄ molecules inside the collapsing bubble or from a heated initially liquid shell.

5. Conclusions

Ionic liquids provide an interesting and unique medium for studies of organic, inorganic, and organometallic syntheses and catalytic reactions. The tunability of room-temperature ionic liquids for specific reactions makes them particularly attractive for synthetic studies.

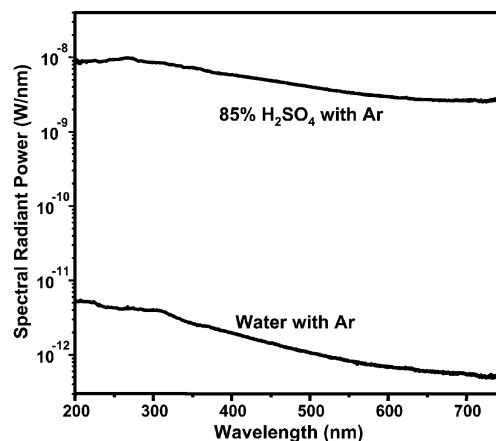


Fig. 5. SBSL emission spectra of 85% H₂SO₄ and water, both degassed with Ar. The intensity of the H₂SO₄ SBSL is ~3000× that of pure water SBSL at the same temperature (295 K).

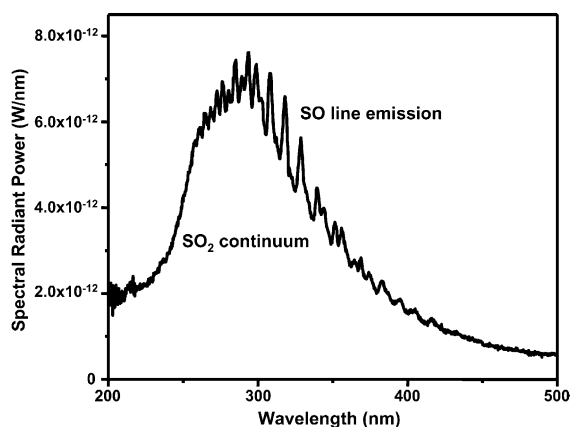


Fig. 6. SBSL emission spectrum of 85% H_2SO_4 regassed with He. Sharp and well-resolved SO lines atop an SO_2 quasicontinuum centered at ~ 300 nm dominate the spectrum.

Recent interest in using ultrasound to drive chemical reactions in ionic liquids has necessitated a better understanding of the effects of ultrasonic irradiation on these solvents. Cavitation (and the subsequent sonochemistry and sonoluminescence) heavily depends on the chemical properties of the fluid medium used. Ionic liquids, molten salt eutectics, and concentrated aqueous electrolyte solutions all provide an interesting approach to control the chemical contents of the collapsing bubble through the reduction of solvent vapor pressure. Chemical control of the vapor content of the collapsing bubble potentially allows for a stronger collapse that leads to greater compressional heating of the volatile reactants. These studies also indicate that the two-site model of cavitation inherently limits the amount of vapor exclusion that can be achieved; regardless of the ultra low vapor pressure of the solvent, sonoluminescence studies show solvent molecules enter the bubble in all of the cases examined. In spite of this limitation, research into the use of ionic liquids provides an interesting method for the study of sonochemistry and sonoluminescence.

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