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Revealing the physicochemical mechanism for ultrasonic separation of alcohol–water mixtures

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The selective separation of ethanol from ethanol–water mixtures by ultrasonic atomization has been reported recently by Sato, Matsuura, and Fujii [J. Chem. Phys. **114**, 2382 (2001)]. In that work, experimental data were reported that confirmed the generation of an ethanol-rich droplet mist and attempted to explain the selective separation in terms of parametric decay instability of the capillary wave formed during sonication. In the present work, an alternate mechanism based on the conjunction theory has been postulated for the process of ultrasonic atomization. This mechanism involves the formation of cavitating bubbles in the liquid during sonication and their eventual collapse at the liquid surface into a cloud of microbubbles that moves upwards in a capillary fountain jet. The selective separation of alcohols has been explained as a corollary effect of the physical mechanism resulting in a surface excess of alcohol molecules formed at the surface of the microbubbles. The alcohol molecules vaporize into the microbubbles and release an alcohol-rich mist on their collapse in regions of high accumulation of acoustic energy.

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INTRODUCTION

Sonochemical effects in liquids for enhancement of reaction rates and chemical degradation have been the topic of many investigators in recent years. The effects of ultrasonic frequency and intensity on chemical reactions and the dependence of ultrasound on temperature and pressure have been reported for various applications. However, very little attention has been paid to the composition of ultrasonically irradiated liquids and aerosol formed. The application of ultrasound in the separation of ethanol–water mixtures has been reported recently.¹ However, a physicochemical explanation could not be provided for the selective separation of ethanol by the investigators.

The process of ultrasonic atomization is generally defined as a result of guided waves of sufficiently high intensity that disintegrate the liquid and form a fine droplet mist with excellent droplet size control. The mechanism for ultrasonic atomization is generally explained by two major hypotheses: *cavitation hypothesis* and *capillary wave hypothesis*. The cavitation hypothesis is generally applied to liquid disintegration in high frequency (> 100 kHz) and high intensity ultrasonic systems or in the study of chemical degradation and kinetic rate enhancement studies by ultrasound. Sollner,² a pioneer in this field, discovered that certain liquids, such as ether, gasoline, water and toluene, atomize at standard pressure and under conditions of reduced pressure while other liquids such as tetralin, decalin, and low viscosity paraffin oil no longer atomize under conditions of reduced pressure. He provided an early explanation for the physical mechanism of atomization based on this disparity in

the behavior of liquids by attributing it to the degassing of the liquid resulting in a reduction in cavitation at lower pressures. He also found that increasing the pressure of the liquid resulted in an increased rate of atomization, while a decrease in temperature of the liquid ceased the atomization activity. This formed the basis for the *cavitation hypothesis* that postulates the formation of hydraulic shocks and the direct ejection of droplets from the liquid surface as a result of the collapse of cavitating bubbles at the liquid surface.

The alternate hypothesis is based on capillary waves that are commonly observed at the liquid surface at high frequencies and explain the formation of droplets as a result of liquid pinching from the crests (peaks) of the capillary wave due to capillary instability. The formation of capillary waves has been photographed by Lang³ and a strong correlation between the droplet size and capillary wavelength favors the capillary wave theory. However, the *capillary hypothesis* is limited to low frequency ultrasonic waves and cannot explain the explosive nature of droplet formation since the capillary wavelength decreases with increasing frequency of ultrasonic irradiation. Thus, the dependence of ultrasonic atomization on liquid degassing, liquid vapor pressure and temperature lends support to the cavitation theory and the observed fountain jet and calculated droplet size favor the capillary hypothesis.

Gershenson and Eknadosyants⁴ conducted detailed experiments on the atomization of a variety of organic liquids and water at a constant intensity and frequency of 2 MHz and defined a parametric ratio, β , where β is the ratio of the liquid saturation vapor pressure to the product of dynamic viscosity and surface tension that lends support to the cavitation hypothesis and provides a measure of the atomization capacity. However, Gershenson and Eknadosyants⁴ did not

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report any experiments conducted with a mixture of liquids. Also, unlike the organic liquids examined, water was found to deviate from a linear relationship between atomization capacity, A , and the parametric ratio, β . This deviant behavior was attributed qualitatively to the anomalous behavior of water responsible for the hydrogen bonding network. Boguslavskii and Eknadiosyants⁵ interpreted the physical mechanism for ultrasonic atomization at high frequencies, such as 2 MHz, with a *conjunction hypothesis*. In this hypothesis, they coupled the cavitation and capillary hypotheses and concluded that incipient cavitation occurs by the formation of at least one cavitating microbubble, which can develop into a cloud of microbubbles. The periodic hydraulic shocks set the surface of the liquid into vigorous oscillatory motion where standing capillary waves of finite amplitude are excited on the surface giving rise to a fountain jet from the surface of the liquid. The microbubble cloud moves upwards in the fountain jet and collapse in the regions of accumulated acoustic energy liberating a fog or mist. The microbubble cloud collapses at points of maximum stress in the fountain jet. Atomization occurs in cycles that depend on the formation of cavitating bubbles and subsequent microbubbles at the threshold input power for atomization. Above this threshold, the number of microbubbles increases substantially resulting in continuous atomization.

The objective of the present work was to provide a physicochemical mechanism for the selective separation of alcohols from alcohol–water solutions by ultrasonic atomization as reported by Sato *et al.*¹ The mechanism of capillary wave formation and ultrasonic atomization proposed by Sato *et al.*¹ is analogous to the capillary hypothesis with the additional premise that selective separation pattern is a result of parametric decay or downconversion of an ultrasonic wave. However, they could not provide a clear explanation for the selective separation of ethanol or detect the capillary wave patterns. Moreover, theoretical estimation with the capillary wave hypothesis shows a negligible difference in droplet sizes between ethanol and water droplets formed by capillary wave instability.

Additionally, to determine if the selective separation mechanism is due to a change in the general dynamics behavior of cavitation, bubble radii versus time were plotted for the ethanol–water system. Figure 1 shows the change in radii for an initial bubble size of 1.5 μm bubble in the presence of water, 10 and 100 mol% ethanol using the Rayleigh–Plesset equation for bubble dynamics. The Rayleigh–Plesset calculations, undertaken in this work, show that the change in surface tension, due to added alcohol, is too small to account for the change in maximum bubble size attained and cannot explain the selective separation during atomization. In this work, the conjunction theory has been applied as the basis for the physical mechanism for ultrasonic atomization and the notion of surface excess of ethanol at the bubble–liquid interface in the capillary jet produces a corollary effect that explains the selective separation.

EXPERIMENTAL WORK

The experimental arrangement illustrating the conceived physical mechanism of atomization in this work is shown in

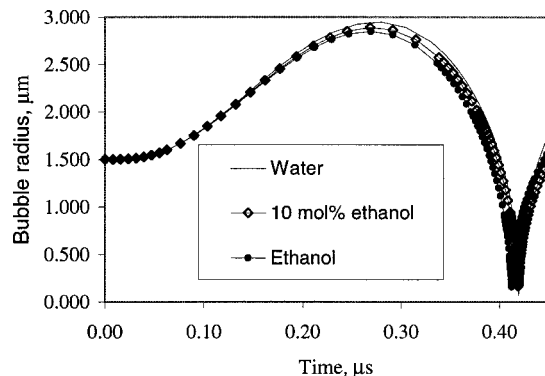


FIG. 1. Radius profile for a single 1.5 μm bubble in the presence of 10% and 50% ethanol, anhydrous ethanol, and water with a power input to the ultrasonic vibrator of 7 W.

Fig. 2. A 20 W sonicator (Honda Electronics) with a maximum power output of 8 W/cm^2 at 2.4 MHz was employed as the source of ultrasound. Experiments were performed in a 1-l glass cylinder. Air was introduced in the glass cylinder for carrying the mist generated during sonication into a collection outlet. The collected mist was then condensed and analyzed using an Abbe refractometer (Leica Mark II Plus). The air rate for blowing the mist into the collection outlet was set to 20 l/min. Experiments performed, in the ultrasonic system, were selected to examine the physicochemical mechanism of sonoseparation. To examine the effect of vapor pressure on the separation process, an ethanol–water and glycerol–water mixture was subjected to ultrasound in the experimental arrangement. Laboratory-grade alcohols and de-ionized water were used in this work. The selective concentration of alcohols to 40 mol% ethanol and 35 mol% glycerol mist, obtained by subjecting 150 ml of 20 mol% of ethanol–water and glycerol–water solution at 25 $^{\circ}\text{C}$ to ultrasonic vibration showed that although glycerol has a higher vapor pressure than water the separation process favors the generation of a glycerol-rich mist.

High-frame rate video at 2000 frames/s captured with a Redlake (PCI-8000S) digital camera showed the formation and rupture of the fountain jet in ethanol–water mixtures. A sequence of images showing the mist formation is illustrated in Fig. 3. An increased rate of mist formation was recorded

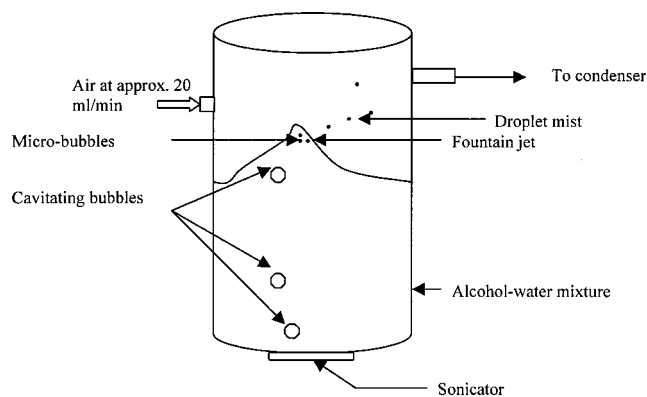


FIG. 2. Illustration of experimental setup for the examination of ultrasonic atomization of alcohol–water mixtures.

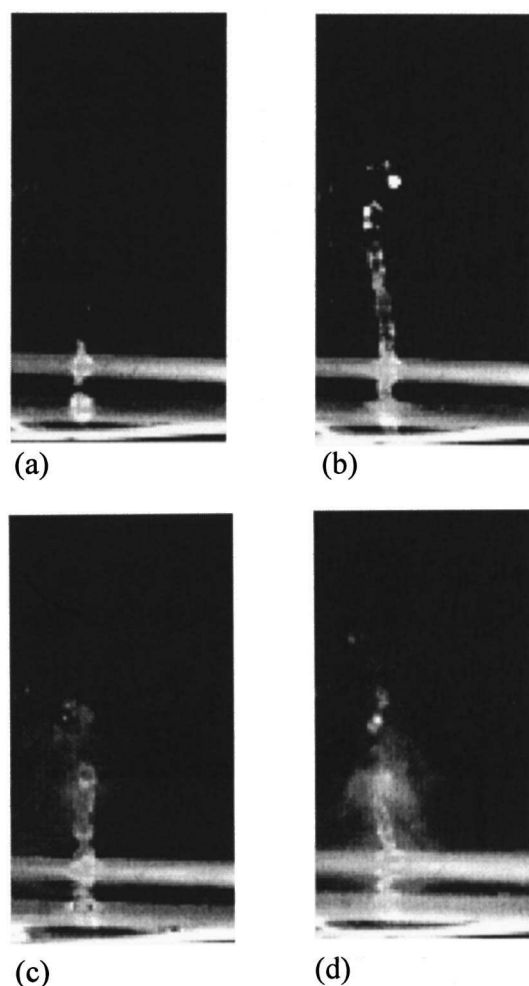


FIG. 3. Images of ultrasonic jet formation and breakup in a 10 mol % ethanol–water mixture, with a power input of 7 W, collected with a high frame rate camera. (a) and (b) Incipient jet formation and capillary rupture at $t=0$ and $t=0.8$ s, respectively. (c) and (d) The jet breakup and resulting atomization at $t=1.3$ s and $t=2.8$ s, respectively.

with increasing ethanol concentration. Intermittent formation of cavitating bubbles observed near the threshold power input, at 7 W, was visually correlated to large ligaments of liquid formed as a result of capillary rupture that created structural defects in the bulk liquid and generated cavitation centers in the sonicating liquid.

The atomization of anhydrous ethanol and glycerol did not occur and a stable fountain jet was formed at low input power levels. Increasing the input power level to the sonicator above the threshold of 10 W or increasing the solution temperature above 30 °C initiated the atomization in both ethanol and glycerol.

Sato *et al.*¹ have provided sufficient experimental data to show an increase in mist concentration during ultrasonic atomization. Experiments performed in this work examine the location at which separation occurs. During the initial period of ultrasonic atomization, samples of ethanol–water were collected from the falling liquid ligaments and were found to decrease in ethanol concentration, while the bulk liquid was at the same concentration as the initial solution. A marked decrease in the bulk solution concentration was recorded af-

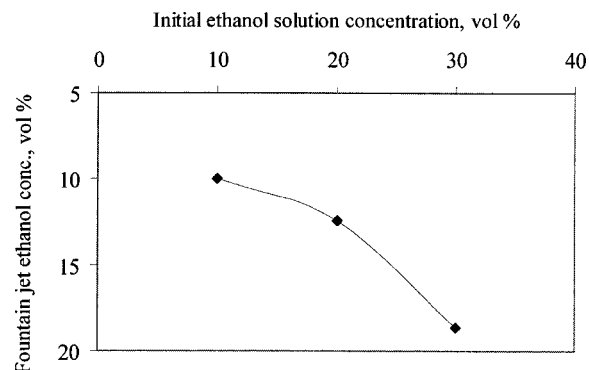


FIG. 4. Reduction in fountain jet ethanol concentration as a function of initial solution concentration.

ter 15 min, indicating that the separation does not occur at the entire liquid surface but only in the fountain jet formed as shown in Fig. 4.

The compression of cavities in the bulk liquid occurs almost instantaneously when they implode during sonication. The ambient liquid around the cavities is significantly cooler and quickly quenches the imploding cavities. Thus a localized hot spot is generated in the solution developing an interfacial region for the vaporization of alcohol into the bubble. Local temperature measurements of the sonicating liquid and the fountain jet formed were made to determine the location of hot spots in the system. The local temperature recorded on the surface of the liquid at the center of the fountain jet was the maximum temperature in the system. The surrounding liquid surface and the bulk liquid were at ambient conditions. However, the temperature of the fountain jet, shown in Fig. 5, was higher than the temperature of the bulk liquid. This phenomenon can be attributed to the rapid quenching of the cavitating bubbles in the bulk liquid. In the fountain jet, such a rapid quenching of microbubbles does not occur providing an extension in the period of time for alcohol vaporization into the bubbles.

RESULTS AND DISCUSSION

The physical mechanism of ultrasonic atomization in alcohol–water mixtures can be explained in terms of microbubble interaction with the fountain jet formed using the

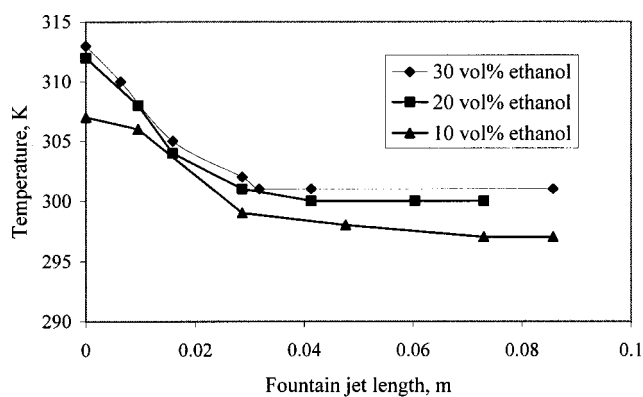


FIG. 5. Temperature of fountain jet as a function of distance from the surface of the irradiated liquid for different concentrations.

conjunction hypothesis. The formation of an alcohol-rich mist is identified by the chemical effects associated with the microbubble cloud generated in this process. The β ratio proposed by Gershenson and Eknodisyants,⁴ can adequately represent the physical effects of cavitation in organic liquids. However, to explain the ultrasonic separation of alcohol–water mixtures, the surface molecular effects governing the separation mechanism must be taken into consideration. In recent work,⁶ spectroscopic, x-ray diffraction and mass spectrometric investigations have been examined for ethanol–water mixtures. With ethanol concentrations of more than 8 mol %, the strong self-association of water molecules is reduced and a large number of ethanol–water bonds are formed and the water–water molecular bonds are broken at higher concentrations of ethanol (>20 mol %). This leads to the formation of a cluster model in an alcohol–water solution consisting of a stacked ethanol core and a thin shell of water. Observed molecular structure has suggested the evolution of an ethanol polymer structure and a complete breakdown of the bulk water structure at the molecular level. Studies related to surface molecular dynamics⁷ have shown that in a 10 mol % ethanol–water solution with an air/solution interface, the redistribution of ethanol molecules at the surface occurs which was initiated from the bulk solution and a depletion layer beneath the ethanol surface excess was reported. Also, previous studies⁸ on ultrasound in alcohol–water mixtures have reported that certain sonochemical processes are influenced by the amount of alcohol adsorbed at the bubble–water interface and not on the type or the bulk concentration of the alcohol in the solution. Hence, the interaction between adsorbed alcohol molecules is reduced as the bubble size is reduced. This leads to the expulsion of some of the alcohol molecules into the bulk solution and the evaporation of alcohol vapor into the bubble. This hypothesis has been extended in the present study to explain the selective separation. The presence of several microbubbles in the jet formed results in the diffusion of alcohol vapor into the microbubbles. The microbubble cloud travels upwards in the jet and collapses in regions of accumulated acoustic energy releasing an ethanol or glycerol-rich mist in an ethanol–water or glycerol–water solution, respectively. In support of this hypothesis, the local temperature recorded in the jet was significantly higher than

the bulk liquid and the liquid surface and the concentration of alcohol in the large liquid ligaments falling off the fountain jet was lower than the bulk or the initial feed solution indicating the separation process occurs in the fountain jet. An intermittent mist formation was observed periodically above the threshold input power level for atomization explained with respect to the formation of cavitation centers on the surface of the fountain jet. An image sequence of the capillary rupture and release of alcohol-rich vapor at threshold input power level is shown in Fig. 3.

At higher temperatures, Sato *et al.*¹ reported a reduction in separation efficiency. Heating the ethanol–water mixture raises the vapor pressure of both ethanol and water above the solution. This increases the β ratio leading to an increase in the atomization rate in both the alcohol and the water and the reduced efficiency of separation. Introduction of air at 20 l/min retains the mechanism of atomization by cavitation cloud collapse in the capillary fountain jet to a capillary pinch-off mechanism at the crests of the capillary waves and formation of the mist that is collected away as product. The convective transport of the mist reduces the probability of altering the jet ambient environment and also assists in the collection of product. This work provides a physico-chemical explanation for the ultrasonic separation of alcohol–water mixtures and forms the basis for further engineering of sono-separating processes.

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