Temperature Effect on the Sonolysis of Methanol/Water Mixtures

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Abstract: Methanol/water mixtures with various concentrations of methanol (from pure water to pure methanol) were exposed to ultrasonic irradiation (724 kHz, 50 W) under an argon atmosphere at various bulk temperatures lying in a range from −30 to +58 °C. It was shown that changing the bulk temperature dramatically influenced the rate of the sonolytic formation of molecular hydrogen. With increasing temperature, the rate initially grows, reaches a maximum, then falls. Increasing the concentration of methanol in the mixture decreases the temperature at which the maximal H_2 formation rate is reached. The observed effect is explained in terms of two opposing factors, and relative contributions of those factors change with the alteration of the bulk temperature: it is suggested that saturating the cavitational bubbles with methanol vapors as the temperature of the mixture being sonicated increases (1) on one hand, accelerates the methanol vapor thermolysis in the cavitational hot spots during the collapse of the bubbles because methanol is a reactant, but (2) on the other hand, decreases the local temperature of the cavitational hot spots that, in turn, disfavor the thermolysis. The effect of the bulk solution temperature on a constant methanol concentration is compared with that of the concentration of methanol in the mixture when a constant bulk solution temperature is kept.

Introduction

Chemical effects of ultrasound on many liquids have been the topic of a large body of research.[1] It has been shown that, when an ultrasonic wave passes through a liquid, the wave's oscillating pressure can cause—under certain conditions—a cavitation phenomenon which involves the generation, growth, oscillations, splitting, and implosions of numerous tiny gas bubbles called cavitation bubbles. The violent and rapid compression of the collapsing bubbles' gas contents leads to the generation of extreme peak local temperatures reaching thousands of kelvins, so-called "sonochemical hot-spots". According to a generally held theory of sonochemical reactions[1]—which is based upon extensive experimental results—it is the thermolysis of gases and vapors in the imploding bubbles that is the primary step to most sonochemical processes.

The reactions induced by ultrasound in methanol/water mixtures of various methanol/water ratios under an argon atmosphere at nearly room temperatures have been studied by a spin-trapping method involving H−D isotope exchange[2] and by quantitative determination of the final sonolytic products.[3] It has been found that methyl radicals, as well as CH_2OH radicals, can be spin-trapped with the total yield of the spin-trapped CH_2OH being much lower than that of CH_3. The final products have been found to be H_2, CH_2O, CO, CH_4, and traces of C_2H_4 and C_2H_6, that is, similar to those observed in the pyrolysis of methanol. The methanol concentration in the methanol/water mixtures has been demonstrated to considerably influence the yields of the trapped radicals and, respectively, those of the final products.

Marked temperature effect on the sonolysis of some various aqueous and nonaqueous liquid systems has been reported previously;[4] as was revealed, the rate of the sonochemical processes either increases or decreases with increasing the temperature (depending on the experimental conditions and on the nature of the system under exposure to ultrasound). One can anticipate that, in the case of methanol/water mixtures, the temperature of the solution being sonicated must significantly affect the process of the sonolysis and, as a result, must influence the product yields. It is of interest to verify this assumption through examining the temperature effect on the sonolysis of methanol/water mixtures. This has still received no study.

The main purpose of the present investigation is an examination of the temperature effect on the hydrogen yield in the sonolysis of methanol/water mixtures with various methanol/water ratios at a wide range of the temperatures.

We chose hydrogen for yield monitoring over other products of methanol sonolysis because (1) it had high yield and could be easily measured by gas chromatography and (2) given the yield of hydrogen, we could estimate yields of other final products of methanol decomposition as well as sonolytic methanol consumption (see the Discussion for a more detailed explanation).

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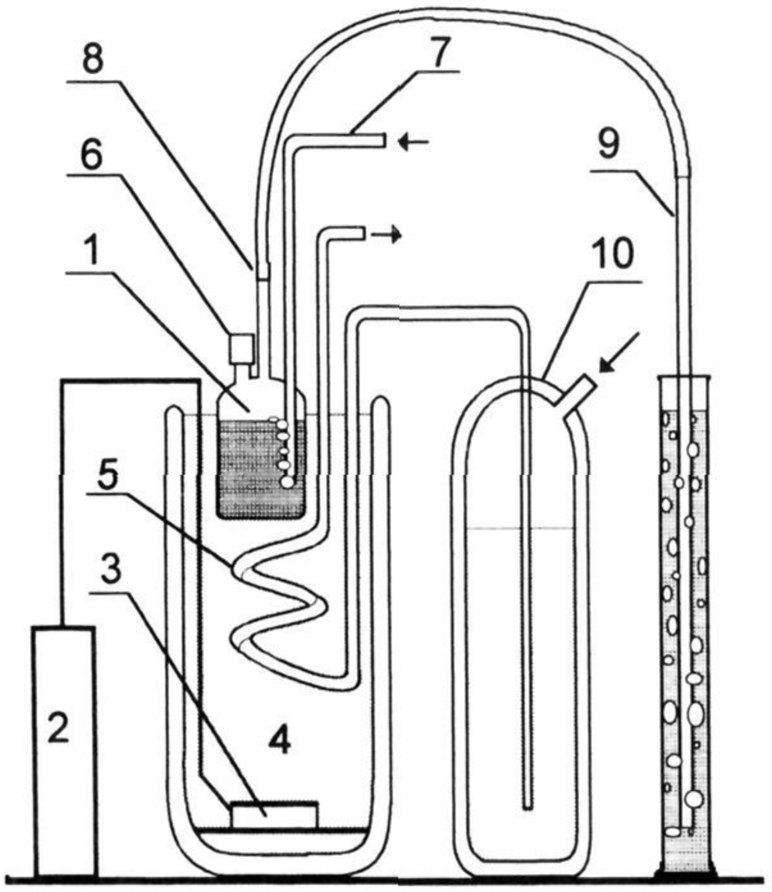

Figure 1. Ultrasonic irradiation setup: (1) sonochemical cell; (2) high-frequency generator; (3) piesoceramic transducer; (4) 1.5 dm^3 Dewar vessel (further referred to as a sonication bath) filled with a vacuum-degassed concentrated aqueous solution of 300 g/dm^3 $CaCl_2$ (freezing point of −48 °C); (5) stainless steel cooling coil pipe; (6) septum for sample taking; (7) argon inlet; (8) argon outlet; (9) glass tube open from below and vertically immersed in a glass cylinder filled with water; (10) Dewar container of liquid N_2.

Experimental Section

The sonication of methanol/water mixtures was performed using a special sonochemical setup that allows temperature maintenance of the liquid being sonicated to range from −30 to +60 °C. It makes sense to describe this setup here in greater detail because sonication in a wide temperature range, especially at low temperatures, may be necessary for many other experimental purposes.

The setup (see Figure 1) includes the following main parts: sonochemical cell, high-frequency generator, piesoceramic transducer, 1.5 dm^3 Dewar vessel (further referred to as a sonication bath) filled with a vacuum-degassed aqueous solution of 300 g/dm^3 $CaCl_2$ (freezing point −48 °C), stainless steel cooling coil pipe, and Dewar container with liquid N_2. The disk-shaped transducer is made of lead titanate−zirconate with a diameter of 32.9 mm, height of 2.8 mm, and main resonance frequency of 724 kHz. The transducer cable connected to the generator is mounted on the bottom of the ultrasonic bath to emit a vertical beam of ultrasound. The coil pipe is immersed in the bath solution of $CaCl_2$. This pipe cools the solution by the evaporation of liquid N_2 propelled from the Dewar container by compressed air. The sonochemical cell, with a total volume of 92 mL, is made of thin glass, has a septum for taking gas samples by syringe technique, a gas inlet with a thin Teflon capillary reaching the cell's bottom for gas bubbling, and a gas outlet. The latter is connected by thin, flexible Teflon tubing to a glass tube open at the bottom which is vertically immersed in a glass cylinder containing water. The glass tube plays the role of gas buffer by using the water column pressure to maintain gas pressure in the cell at slightly higher than atmospheric pressure.

In the experiment we tested a series of methanol/water mixtures with the following mole fraction of methanol (mfm),[5b] the corresponding concentration of methanol in the units of mol/dm^3 at 20 °C being indicated in round brackets: 0.0 (0.0), 1.8 × 10^{-3} (0.1), 1.8 × 10^{-2} (1.0), 0.11 (5.5), 0.25 (11), 0.40 (15.5), 0.62 (20), 0.75 (22), and 1.0 (24.7). The experiment was performed as follows: A 40 mL portion of methanol/water mixture with a given methanol concentration was placed in the cell and immersed in the ultrasonic bath at room temperature. Then the argon flow (90 mL/min) was started, which produced vigorous bubbling of the mixture. The saturation with argon prior to the first sonication was done for 20 min.[6] Compressed air was then delivered into the Dewar container to propel liquid N_2 into the coil pipe. When the liquid in the ultrasonic bath reached a temperature of −30 °C, the pressure in the Dewar container was released, stopping the propulsion of liquid N_2, thus ending the cooling process. The system was left to stand for 10 min to reach a temperature equilibrium between the bath and the cell. Next, the cell was sonicated for 1 min. As had been measured calorimetrically in preparatory experiments, the transducer's acoustic power output was 45 ± 5 W.[7] The temperature in the bath did not influence the anode current in the high-frequency generator tubes, evidencing a uniform acoustic power output over the whole investigated temperature range. Sonication was accompanied by the formation of an ultrasonic fountain (approximately 3−4 cm in height) and a dense fog in the cell. After the 1 min sonication was completed, a 0.5 mL gas sample was taken and analyzed by gas chromatography for H_2.[8] The cell was then taken out of the bath and again bubbled with argon flow for 5 min to remove the accumulated hydrogen (note that there was no contact of the cell's contents with air during the whole experiment). The bath's temperature was increased 5−10 °C degrees with the immersion of an electric heater. The cell was then put into the bath again and left to stand for 10 min to reach a temperature equilibrium. Again, the cell was sonicated for 1 min with subsequent analysis of the cell's contents for H_2. This procedure, including the temperature rise, argon bubbling, sonication, and H_2 yield determination, was repeated 4−9 times to obtain 5−10 temperature/hydrogen yield data points for each examined methanol concentration.[9]

Results

Figure 2a,b illustrates the temperature dependencies of the H_2 formation rate in the sonolysis of methanol/water mixtures at various concentrations of methanol. The curves for 1.8 ×

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(5) (a) *Fizicheskie velichiny. Spravochnik (Physical Values. Reference Book)*; Grigor'ev, I. S., Melikhov, E. Z., Eds.; Energoizdat: Moscow, 1991. (b) Concentrations of methanol in the methanol/water mixtures are expressed in the units of mole fraction of methanol (mfm) throughout the paper.

(6) To guarantee that the procedure of saturation did not significantly alter the methanol/water ratio due to evaporation of methanol, the solution was checked gas chromatographically after the 20 min bubbling was conducted, as described above, decreasing the concentration of methanol in methanol/water mixtures at any initial methanol/water ratios at 49 °C by less than 5%.

(7) The transducer's acoustic power output was measured as follows: A glass bulb with a thin polyethylene film bottom that was perfectly transparent to ultrasound was filled with a measured amount of water (about 250 mL) at room temperature. The bulb was immersed in the ultrasonic bath so that only the bulb's bottom touched the liquid in the bath. The generator was switched on for a certain period of time. The water's temperature in the bulb before and after sonication was measured with a precise thermometer. Given the sonication time, the rise of temperature due to the sonication, the mass of water in the bulb, and the specific heat capacity of water, we calculated the acoustic power dissipated as heat in the bulb. Note that an overwhelming part of the energy of ultrasound converted into heat—this assumption can be easily verified by comparing the energy that resulted in heat with that which went into the decomposition of water (the latter can be estimated from the hydrogen yield, see the Experimental Results). It also must be mentioned that the formation of an acoustic fountain on the surface of water in the bulb prevents the ultrasound beam from reflection from that surface. Using various sonication times (lying in the range from 20 s to 1 min), we obtained the same value of acoustic power, which evidenced that losses of heat from the bulb during the sonication could be neglected. To make sure the entire beam of ultrasound reached into the bulb, we sequentially placed a series of porous rubber diaphragms with round holes of gradually decreasing diameters through which the beam of ultrasound had to penetrate to reach the bulb. The smallest hole not causing decrease in measured power dissipated in the bulb was found to have a diameter of 2.2 cm (i.e., the lagest possible diameter the ultrasound beam could have was 2.2 cm), which was much less than the diameter of the bulb's bottom. Thus, the measured acoustic power dissipated as heat in the bulb could be regarded as the overall acoustic power irradiated by the transducer. Additionally, this simple diaphragm technique allowed us to make a rough estimation of the intensity of ultrasound in the beam, which was found to be about 12 W/cm^2.

(8) Gas chromatography conditions. Column: length 1 m, diameter 4 mm, filled with molecular sieves with average pore size 4 Å. Column temperature: 60 °C. Carrier gas: Ar, 25 mL/min. Detector: based on thermal conductivity (katharometer). Gas sample volume injected: 0.5 mL.

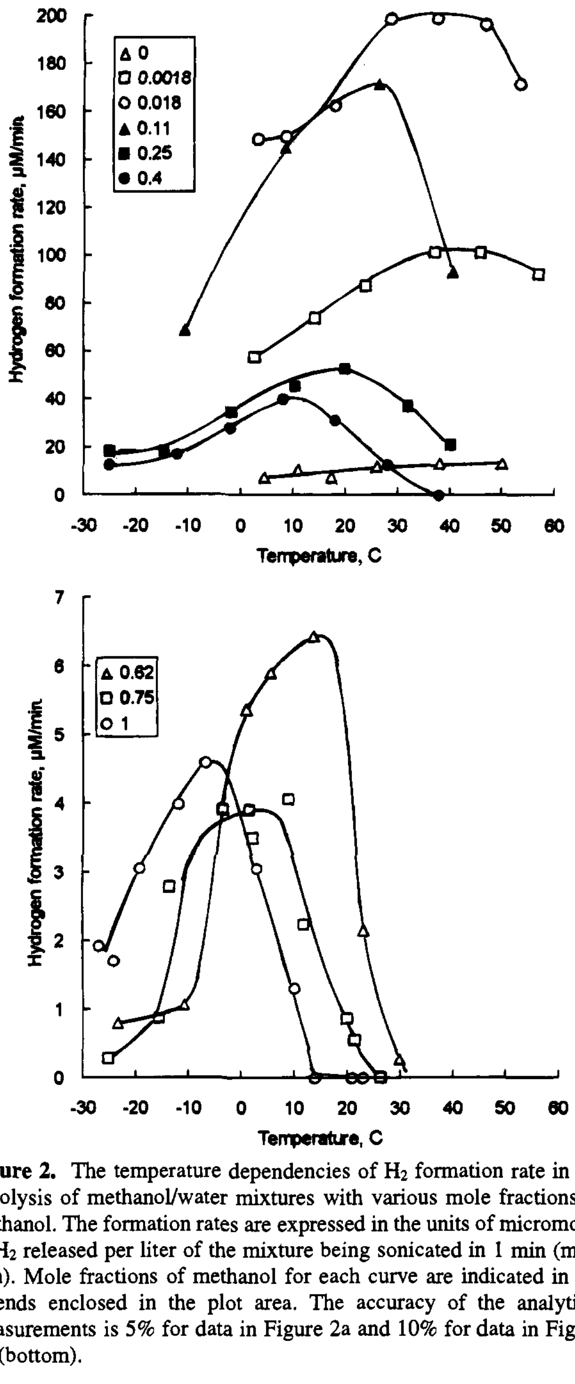

Figure 2. The temperature dependencies of H_2 formation rate in the sonolysis of methanol/water mixtures with various mole fractions of methanol. The formation rates are expressed in the units of micromoles of H_2 released per liter of the mixture being sonicated in 1 min (mM/min). Mole fractions of methanol for each curve are indicated in the legends enclosed in the plot area. The accuracy of the analytical measurements is 5% for data in Figure 2a and 10% for data in Figure 2b (bottom).

10^{-3}, 1.8 × 10^{-2}, 0.11, 0.25, and 0.40 mfm methanol/water mixtures and for pure water are plotted in Figure 2a, and the ones for 0.62, 0.75, and 1.0 mfm mixtures are plotted in Figure 2b (with a larger *Y*-axis scale). It can be seen in the figure that the curves for 0.11, 0.25, 0.40, 0.62, 0.75, and 1.0 mfm mixtures look similar, the rates of H_2 formation being maximum at certain temperatures and considerably lower at both lower and higher ones. The curves for pure water and 1.8 × 10^{-3} and 1.8 × 10^{-2} mfm mixtures show less sharp temperature/H_2 yield relationships, and in case of pure water, the curve has no clearly defined point of maximum H_2 formation rate at all. The absolute values of hydrogen formation rates and the temperatures at which the maximal rates are observed depend on the methanol concentration in the mixtures being sonicated. It is clearly seen that decreasing the methanol concentration, figuratively speaking, "shifts" all curves as a whole (including the points of maximum H_2 formation rates) from the lower temperatures to the higher and makes the temperature dependencies less sharp. The maximum H_2 formation rates reached in mixtures with different methanol concentrations differ quite considerably: in the 0.75 mfm mixture, it is about 50 times less than that of the 1.8 × 10^{-2} mfm. Notice that, for 0.40, 0.62, 0.75, and 1.0 mfm mixtures, the temperature thresholds are observed: that is, the greater temperatures, no detectable hydrogen is produced. The thresholds lie at greater temperatures for less concentrated methanol solutions. One can suppose the thresholds exist for the pure water and 1.8 × 10^{-3}, 1.8 × 10^{-2}, 0.11, and 0.25 mfm mixtures as well, but they probably lie beyond the range examined in this experiment.

Discussion

Thus, the experimental findings of the present study reveal dramatic and peculiar H_2 yield/temperature relationships. One can consider the hydrogen yield as a rough measure of sonolytic methanol decomposition since the rate of H_2 formation is roughly proportional to the sum of the formation rates of all main carbon-containing products in the sonolysis of methanol/water mixtures (see ref 3). In addition, note that, even in mixtures with as little as 1.8 × 10^{-3} mfm, the yield of H_2 is about 6 times greater than that in pure water. Therefore, one can suppose that, even in diluted methanol solutions, it is the decomposition of methanol that makes the most significant contribution into the formation of hydrogen.

Before going into a discussion of this experiment's results, let us first consider in more detail the results of the previous methanol/water mixture sonolysis investigations[2,3] cited in the Introduction. These investigations revealed the following outstanding feature: yields of spin-trapped CH_3 radicals, as well as those of hydrogen and all the detected carbon-containing final products, have been shown to depend similarly upon the concentration of methanol in the methanol/water mixture. By increasing the methanol concentration, yields initially grow, reaching a maximum at roughly 2−5 M methanol, and fall to almost zero in pure methanol. In explaining why the methanol concentration influences the yields as it does, the authors of both these works invoke the following two opposing effects: they suppose that (1) on the one hand, with increasing methanol concentration, the yields first increase, as methanol is a reactant (apparently, the higher the concentration of methanol in the mixture, the more methanol vapors in the bubbles where the vapors undergo the thermolysis at the moment the bubbles collapse) and (2) on the other hand, having lower specific heat capacity ratios (C_p/C_v) than that of argon, methanol vapor, in accordance with thermodynamic laws, decreases the peak local temperatures reached owing to the compression of the gas in the collapsing cavitation bubbles, which, in turn, decreases the rate of thermal methanol decomposition.

As does the methanol/water ratio, the temperature of the whole solution being sonicated must evidently influence the concentration of methanol vapors in the cavitation bubbles. For instance, the equilibrium vapor pressure of pure liquid methanol at −29 °C is 0.5 kPa, while that at +29 °C is 20 kPa, which is 40 times greater.[5a] If one takes into account the rate of methanol evaporation from the bulk into cavitation bubbles having life

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(9) In the experiment, we actually measured the temperature in the bath rather than in the cell. However, it had been checked previously that 10 min was enough to reach a temperature equilibrium between the bath and the cell. During each 1 min sonication, as revealed by preparatory experiments, the temperature in the cell grew by 4−6° owing to losses of the ultrasound energy that, for the most part, converted to heat. Rise in temperature due to the energy loss could not be compensated without considerably complicating the setup, but as time dependencies of the temperature in all cases were almost linear and uniform, it could be assumed that the temperature of the sonication was the mean of the temperatures in the cell before and after the sonication.

expectancies as short as 10−100 periods of ultrasonic wave pressure oscillations ($10^{-5}-10^{-4}$ s for our experimental conditions), the assumed difference must evidently grow still further. In addition, not only methanol vapors but water vapors as well must contribute to lowering the peak temperatures in the bubbles—the contribution of the water vapors being more significant in less concentrated methanol solutions and at greater bulk temperatures.

Therefore, the dramatic H_2 yield/temperature relationships revealed in the present study can, at first glance, be easily explained in terms of the same two opposing effects as can the product yield/concentration relationships discussed above. That is to say, increasing the bulk temperature, on one hand, facilitates the methanol sonolysis by increasing the reactant concentration in the bubbles; at the same time, the greater bulk temperatures disfavor the sonolysis through reducing the peak local temperatures in the collapsing bubbles by virtue of saturating the gaseous mixture in the bubbles with vapors having a low C_p/C_v ratio.

Suslick *et al.*[4a−c] studied the effect of solvent vapor pressure on the rates of two sonochemical reactions conducted in alkane solutions, (1) the bleaching of diphenylpicrylhydrazyl (DPPH) and (2) and the decomposition of $Fe(CO)_5$ where the solvent pressure being altered by varying both the composition of the solvent (i.e., the ratio of alkanes with different vapor pressures in the solvent mixture) and its ambient temperature. For both reactions, it was revealed that the greater the solvent vapor pressure, the less the sonochemical rate. Good linear correlation was found between the logarithm of the sonochemical rate and the solvent vapor pressure. It was supposed that increasing the solvent vapor pressure diminishes the maximum temperature reached in the collapsing cavitation bubbles. Later, Suslick and co-workers[4d] determined the first-order rate coefficients of sonochemical ligand substitution as a function of metal carbonyl vapor pressure. They sonicated alkane solutions of metal carbonyls ($Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$) in the presence of excess triphenylphosphine at various ambient temperatures in alkane solutions. In doing so, the solvent vapor pressure was kept constant at all chosen ambient temperatures by properly varying the alkane mixture solvent composition. It was revealed that the higher the ambient temperature, the more rapid the sonochemical reaction rate; the observed first-rate constants were shown to depend linearly on the carbonyl vapor pressure. It should be noted that the carbonyl vapor pressure was roughly 30 times less than the solvent pressure; therefore, the carbonyl vapors' influence on the process of cavitation could be neglected. Hence, one could suppose the peak temperatures in the collapsing bubbles to be almost the same at different ambient temperatures in the solutions under sonication. Thus, if one looks at the results of the two above-mentioned experiments by Suslick *et al.* from the viewpoint of the effect of the ambient temperature on the rate of sonolysis, they will see that the two counteracting factors influencing the sonochemical rate, where both grow with increase of ambient temperature, have been isolated and studied separately: (1) the decrease of the peak temperature reached at the moment of the cavitation bubbles' collapse and (2) the increase of the reactant's concentration in the hot-spot area.

In the case of methanol/water mixtures examined in the present study, it is impossible to separate the two above-mentioned factors since methanol plays the role of both a reactant and a solvent, making a significant contribution to the bubbles' gaseous contents and considerably influencing the peak temperature of cavitation. This possibly explains why we found no simple relationship between the rate of hydrogen formation, and either (1) the vapor pressure of methanol, or (2) that of water, or (3) the total vapor pressure in the methanol/water mixtures.

Despite the fact that the above given explanation for the temperature effect observed in our experiment in terms of two opposing factors seems to be good enough, one can readily see from the experimental results that varying the bulk temperature in a constant methanol concentration is not the full equivalent of varying the concentration of methanol in the mixture at a constant bulk temperature, though obviously one could obtain the same methanol vapor pressure in the bubbles both in less concentrated methanol solutions at the greater temperatures and, vice versa, in more concentrated ones at the lower temperatures. For instance, as is evident in Figure 2, the maximal H_2 production rate that can be reached in pure methanol is still roughly 40 times less than that in the 1.8×10^{-2} mfm methanol/water mixture. This fact cannot be explained simply in the framework of the interplay between the pressure of the methanol vapors and peak temperatures in the bubbles. It seems likely that, in a more detailed explanation, the influence of physical properties of the solution on the process of cavitation itself must be invoked.

Conclusions

It was revealed in the present investigation that a variation of temperature causes dramatic changes of H_2 formation rate in the sonolysis of methanol/water mixtures under an argon atmosphere; the effect of the temperature in a constant methanol concentration bears a general resemblance to that of a methanol concentration in a mixture at a constant temperature. It was shown that, for each given composition of the mixture, a temperature for maximal H_2 formation rate exists and both lowering and raising the temperature causes significant decrease in the rate of hydrogen formation—the greater the concentration of methanol, the higher the temperature of the maximum. The revealed temperature effect can be explained in terms of two opposing effects: saturating the cavitation bubbles with methanol vapors while increasing the temperature (1) on one hand, favors the sonolysis (as methanol is a reactant), but (2) on the other hand, reduces the peak temperatures at the cavitational hot spots, which decreases the rate of methanol thermolysis. However, to explain it more fully, the influence of the temperature on the cavitation process must be taken into consideration. The discovery of a dramatic increase in the rate of the sonolysis of pure methanol at approximately −8 °C, as compared to that observed at nearly room temperatures, opens the way to the study of the sonolysis of pure methanol, which was practically impossible previously. Without a doubt, it is necessary in future investigations to examine the changes in the full composition of the final sonolytic products in the sonolysis of methanol/water mixtures at various bulk temperatures, as this can give much important data on the conditions at the cavitational hot spots.

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