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Harisinh B Parmar
Curtin University

Yusuke Asakuma
University of Hyogo

Chi Minh Phan
Curtin University

Geoffrey M Evans
University of Newcastle

Langmuir

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Influence of Microwaves on the Water Surface Tension

Harisinh Parmar,[†] Masahiro Asada,[‡] Yushin Kanazawa,[‡] Yusuke Asakuma,[‡] Chi M. Phan,*[,†] Vishnu Pareek,[†] and Geoffrey M. Evans[§]

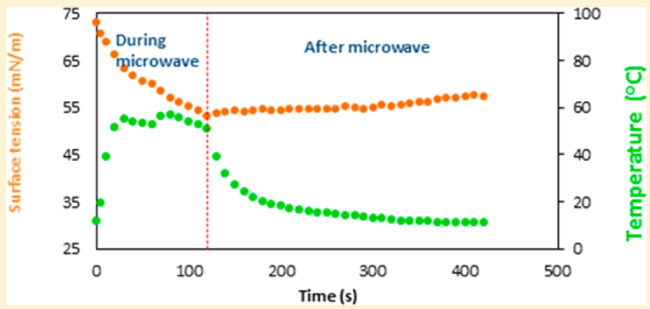
[†]Centre for Process Systems Computations, Curtin University, Perth, Washington 6845, Australia

[‡]Department of Mechanical and Systems Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

[§]Department of Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia

Supporting Information

ABSTRACT: In this study, microwave irradiation was applied to hanging droplets of both water and ethylene glycol. Once the irradiation had ceased and the droplet was allowed to return to its original temperature, it was found that the surface tension of ethylene glycol returned to its original value. In contrast, the water surface tension remained well below its original value for an extended period of time. Similar observations have been reported for magnetically treated water, but this is the first time that such a lasting effect has been reported for microwave irradiation. The effect can be attributed to the unique hydrogen bonds of interfacial water molecules. While the irradiation intensities used in this study are well above those in household devices, there is certainly the potential to apply the methodology to industrial applications where the manipulation of surface tension is required without the use of chemical addition.



■ INTRODUCTION

Water is a diamagnetic solvent and can be levitated in air by a magnetic field.[1] Water can also retain "lasting" effects in scaling,[2] pH,[3] electrolytic potential,[4] and surface tension[5,6] after magnetic field exposure. Interestingly, this lasting effect occurs only when the water is in motion relative to the magnetic field. Since microwave irradiation provides a similar set of conditions with electromagnetic oscillations, one might also expect similar effects with microwaves.

Microwave irradiation is well known for the heating of water, which occurs as a result of dipolar polarization, ionic conduction, and interfacial polarization.[7] Since the water surface tension decreases with increasing temperature,[8−11] microwave irradiation expectedly lowers the surface tension during heating. On the other hand, nonthermal effects of microwave irradiation on water are not well understood in spite of reported effects on aqueous reactions in the literature. Earlier studies[12,13] have suggested that the enhanced rates of aqueous reaction were caused by the nonthermal effects of microwave irradiation. Consequently, there have been a number of experimental results in different aqueous reactions.[14,15] Microwave irradiation can dramatically increase the yield of the Leuckart reductive amination from 2 to 95%.[16] Higher yields and selective reactions have also been extensively reported in aqueous polymerization.[17,18] The synthesis of polypeptides was also improved with microwaves by a factor of 100.[19] Emulsion polymerization, e.g., styrene polymerization in potassium persulfate as an initiator and sodium dodecyl sulfonate,[20] was also enhanced by microwaves. A detailed analysis, between microwaves and conventional heating, pointed to an increased decomposition rate of potassium persulfate by a factor of 2.4 with microwaves. The anaerobic digestion of sludge was also significantly improved with microwave treatment.[21]

Summarily, microwave irradiation has been reported to enhance reaction rates and yields. However, the underpinning mechanism for these influences remains unknown. This study reports experimental investigations of microwaves on the surface tension. Consequently, the in situ results can provide new insights into the reportedly enhanced effects on aqueous processes by microwaves.

■ EXPERIMENTAL SECTION

Simple heating was carried out in a cubic cell ($2 \times 2 \times 2$ cm^3) with different water volumes (0.8 and 2 mL). The temperature was monitored as a function of time during and after microwave irradiation in order to characterize the influence of microwave heating on the air/water interface

The surface tension was measured using the pendant drop method. A liquid drop was formed at the tip of a 1.4-cm-long sample of polytetrafluoroethylene (Teflon), with an inside diameter of 1 mm and a wall thickness of 0.5 mm. The tube was placed inside the reactor, which is microwave-proof. After droplet formation, an optic fiber was inserted inside the droplet. Some water was left at the bottom of the reactor to ensure that the air is saturated with vapor (Figure 1). The light source and diffuser were positioned on one side of the reactor. A

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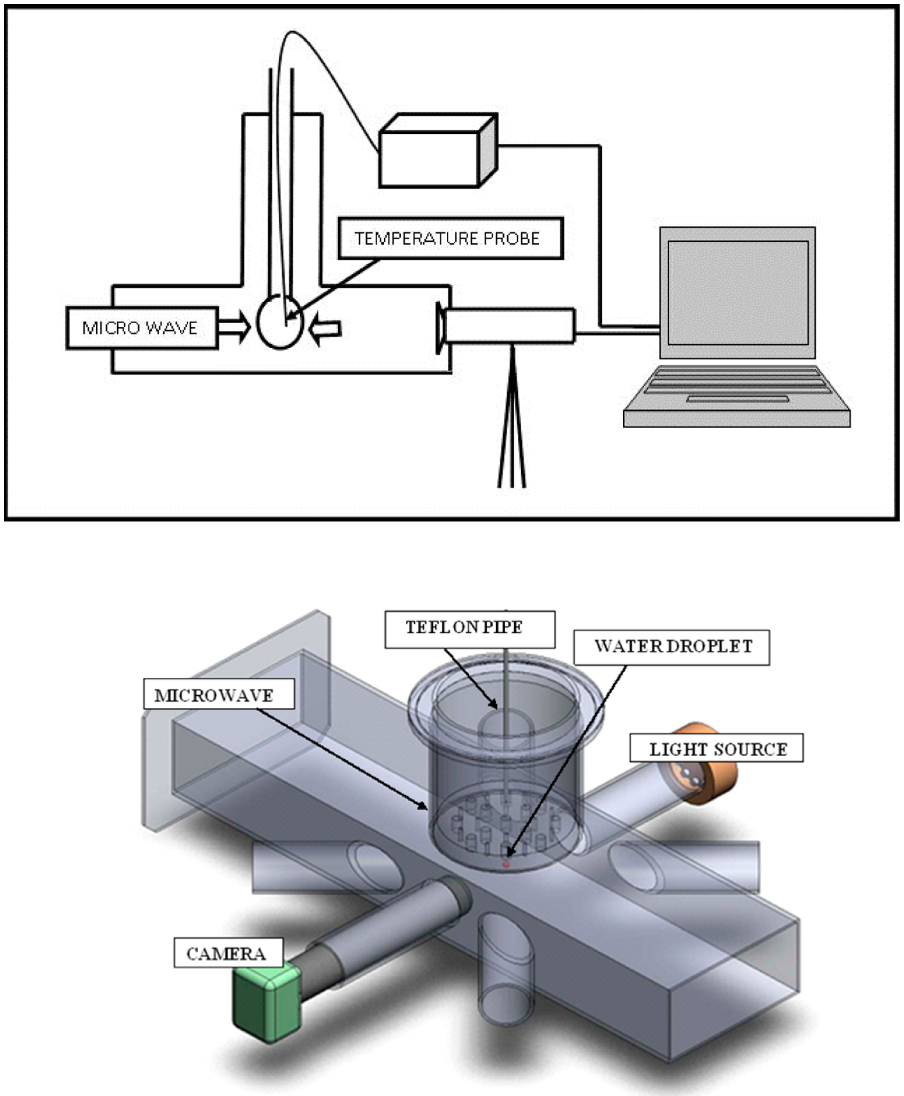

Figure 1. Side and 3D views of the experimental apparatus.

digital camera (Sigma Koki Co., LTD model SK-TC202USB-AT) was employed from the opposite side to capture the shape of the droplet during and after microwave radiation.

It is noteworthy that Teflon has been used in a microwave study[22] at higher temperature (>200 °C) and no contamination was reported. The fiber, FS100 (Anritsu Co., Japan), was also designed for microwave applications. In addition to deionized water, ethylene glycol 99.5% (Kanto Chemicals Co., Japan) was also tested.

The temperature inside the droplet both during and after microwave irradiation was transferred to the computer via a digital controller (Anritsu meter Co., LTD; model FL-2000). Images of the droplet were recorded with a digital camera. The edge profiles of the droplet were analyzed by axisymmetric drop shape analysis (ADSA) to calculate the surface tension.[23] Examples of a raw image and fitting results are shown in Figure 2. It is noteworthy that the ADSA software finds the surface tension by fitting the whole droplet profile (Figure 2b) and is independent of the droplet size.[24]

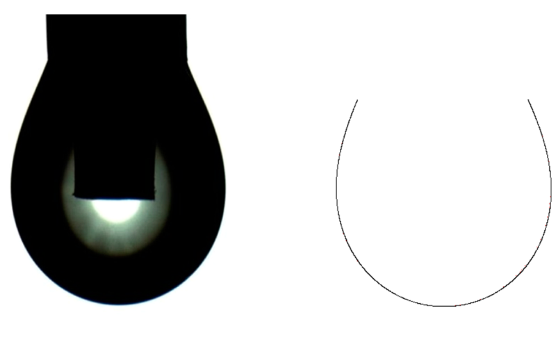

Figure 2. Drop profile: (a) raw image and (b) edge for surface tension measurement.

■ RESULTS

Heating of Water. The heating experiments demonstrated the significance of the air/water interfacial zone in the heating process (Figure 3): the larger volume (2 mL) was heated faster than the smaller volume. The 2 mL of water was visually boiling (Figure 4) after 1 min, whereas the smaller volume was not. The results contradicted the normal expectation; that is, a larger volume takes a longer time to heat. The results can be explained by considering the air/water interfacial zone. Because the surface water molecules have only three hydrogen bonds,[25] the friction in the interfacial zone is expectedly less than that in the bulk (in which water molecules have four hydrogen bonds).

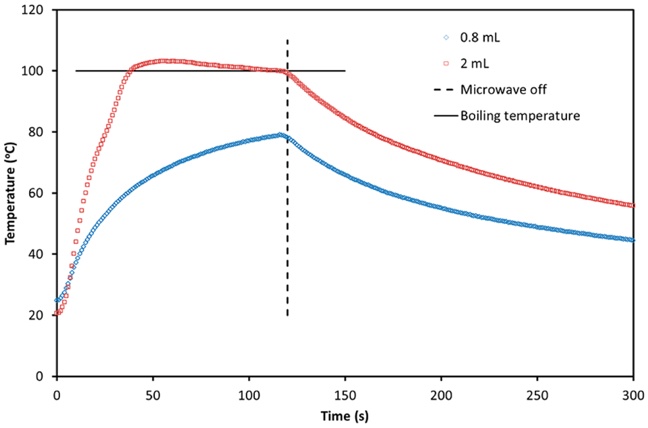

Figure 3. Temperature profiles of microwaves heating a cubic cell.

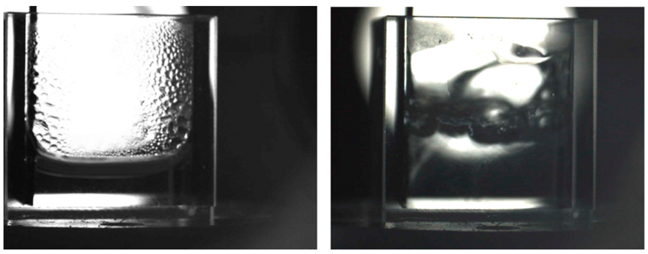

Figure 4. Microwave heating of the water in a quartz container after 1 min at 600 W: (left) 0.8 and (right) 2 mL of water.

Hence, the interfacial water can strongly absorb microwaves without being heated. Since the 0.8 mL volume has a larger surface/volume ratio than the 2 mL volume, 5 versus 2 cm^{-1}, the heating was less effective. The changes in the interfacial zone should be revealed by the in situ surface tension, which is directly related to the molecular structure of the interfacial zone.

Surface Tension of Water. Figure 5 shows the surface tension and temperature of a water droplet as a function of time. During microwave irradiation, the temperature increased as expected. Generally, the temperature reached a plateau within about 20 s and remained at that temperature until the microwave irradiation was turned off at 120 s. At that time, the droplet gradually returned to its original temperature within 400 s. With the pendant drop setup, the water volume was <0.2 mL with a surface/volume ratio of ~20 cm^{-1}. As a result, the temperature was limited to ~60 °C. During microwave irradiation, the surface tension reduction was approximately proportional to the irradiation intensity. Once irradiation had ceased, the surface tension gradually increased, but unlike the temperature, it did not return to its original value.

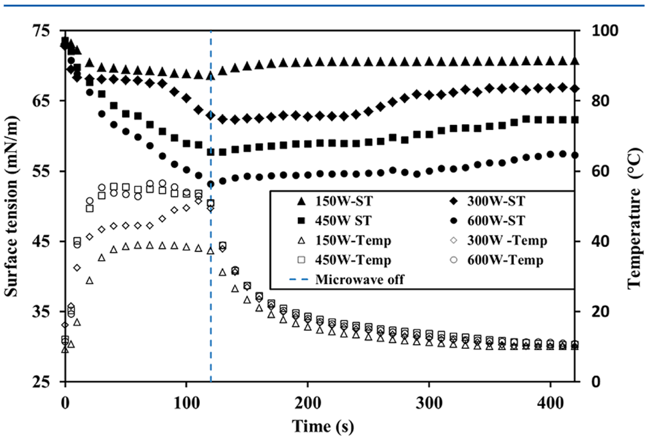

Figure 5. Surface tension and temperature vs microwave intensity and irradiation time (solid symbols, surface tension; unfilled symbols, temperature).

Surface tension was plotted against temperature as shown in Figure 6. It should be noted that the literature surface tension

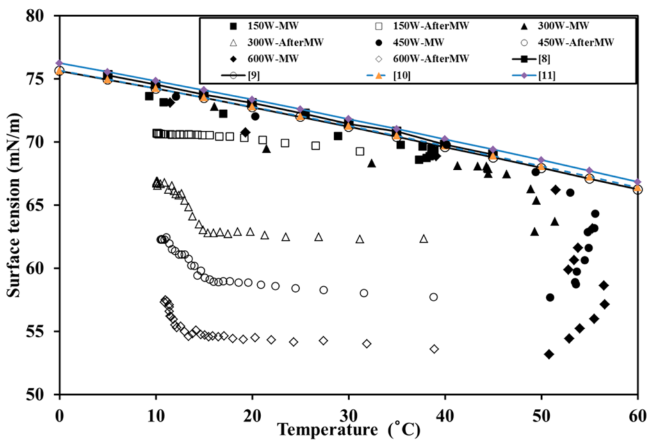

Figure 6. Surface tension vs temperature (solid symbols, during irradiation; unfilled symbols, after irradiation; and lines, literature values[8−11]).

was obtained for homogeneous systems; that is, the liquid and vapor phases have the same temperature.[8−11] During the heating and cooling periods in this study, in contrast, the system was expectedly nonhomogenous, in which the droplet temperature was significantly higher than the air temperature. At the beginning of microwave heating, however, the surface tension and temperature followed the reported relationship in the literature. After that, the surface tension drops much further than the theoretical curves, especially above 50 °C. It is noteworthy that to have a surface tension lower than 60 mN/m the droplet temperature would be higher than the boiling temperature.[9,11] On the other hand, boiling was not observed during our experiments.

The results indicated that the surface tension reduction is not due solely to a thermal effect. During microwave irradiation, the surface tension may be influenced by convection within the droplet and Marangoni surface flow. However, these effects were eliminated once the microwave irradiation was turned off. The data after microwave irradiation clearly demonstrated the lasting effect on the surface tension. The data in Figure 5 also indicate that surface tension would return to its normal value eventually. However, the normalization time would be more than 1 h under these conditions.

The temperature profile of the water droplet was also modeled on the basis of conventional heat loss equations.[26] Once the 600 W microwave is turned off, it can be assumed that the water droplet has a uniform temperature of 51 °C. Consequently, the droplet was cooled due to heat loss to the surrounding air (at 21 °C). The one-dimensional partial differential equation for a sphere was solved to get the temperature at the surface (continuous curve in Figure 7). Detailed modeling and assumptions are provided in Supporting Information. The experimental temperature closely followed

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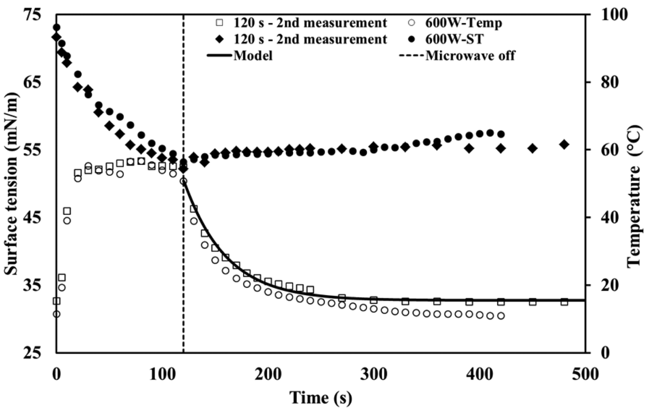

Figure 7. Repeated measurements at 600 W irradiation intensity and the temperature profile calculated from modeling.

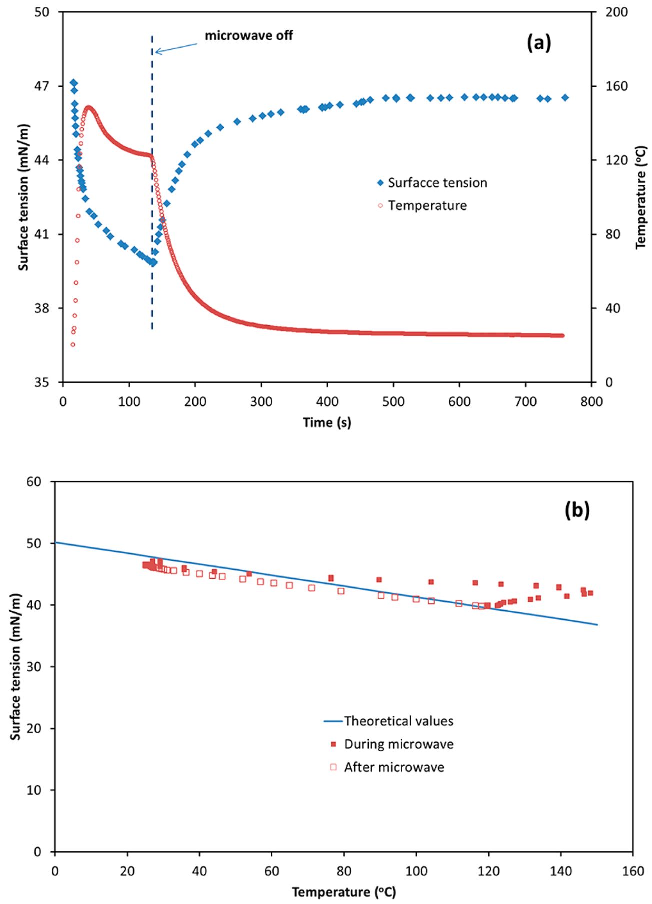

Figure 8. Ethylene glycol under microwave irradiation: (a) transient surface tension and temperature and (b) relationship between surface tension and temperature during and after microwave irradiation.

the modeled prediction, without any fitting. Moreover, the influence of heat flux at the surface, if any, was diminished after 3 min (when the droplet temperature was the same as the temperature of the surrounding air). Summarily, the experimental measurements have clearly indicated a lasting influence of microwave irradiation on the water surface tension that cannot be explained by heat loss or evaporation at the water surface.

Surface Tension of Ethylene Glycol. An ethylene glycol (EG) droplet was also investigated using the same procedure. The surface tension of ethylene glycol (Figure 8) was reduced during microwave heating as expected. However, the surface tension quickly recovered during the cooling period (within 4 min after the microwave was turned off). Except for a few measurement points at the beginning of microwave radiation, the surface tension/temperature plot (Figure 8b) closely followed the reported data in the literature.[27] Hence, it can be concluded that the surface tension reduction of EG was purely due to the thermal effect of the microwave. The sharp contrast between Figures 8b and 6 highlighted the fact that the lasting effect of microwaves on water is not due to simply thermal effects.

■ DISCUSSION

The surface tension of water and other solvents strongly depends on hydrogen bonding. Among common organic solvents, ethylene glycol has a relatively high degree of hydrogen bonding, which results in a high surface tension, ~48 mN/m.[28] In contrast, the surface tension of other solvents, such as methanol and ethanol, is only ~23 mN/m. The results with ethylene glycol indicated that the lasting effect is not expected with other solvents. Consequently, the lasting effect in surface tension is probably unique to water.

In addition to strong H bonding, water also has an asymmetric arrangement at the interface. The relatively high surface tension of water, 72 mN/m, can be attributed to the complicated arrangement of hydrogen bonding in the interfacial zone. A previous study on surface water has shown that the outmost layer of the water molecules has a 25% unfulfilled hydrogen bonding capacity,[25] with a corresponding surface energy of 67 mN/m. Molecular simulations have shown that the interfacial water contains at least three distinctive layers, namely, the fully-bonded molecules in the bulk, 75% bonded molecules on the outmost layer, and any other state(s) in between.[29] Our recent study has indicated that the water arrangement at the interface, i.e., H bonds, is the main factor controlling the surface tension, even in the presence of strong surfactants.[30] Collectively, these studies indicated that the water surface tension is determined by the H-bond network between interfacial water molecules. The H-bond network at the interface depends on the dynamics of H-bond forming and breaking,[31] which is directly related to the rotational motion of the water molecules. More recently, it has been shown that the H-bond switching for surface water is 3 times slower than that in the bulk.[32] The heating experiment indicated that water surface molecules absorb a significant quantity of microwave energy without being heated.

We hypothesize that the water surface tension was lowered by microwaves in a similar manner to that after exposure to a magnetic field.[6] Although the exact mechanism is not well explained, it appears that magnetically treated water molecules exhibit a slower rotational motion and stronger H bonds,[6] thus affecting the air/water interfacial tension.[33] If the microwave-irradiated water also has a slower rotation and stronger H bonds, then the surface tension would be expectedly lower. Alternatively, the surface tension could be lower because the dynamic switching of H bonds at the interface is faster after microwave treatment. Previous studies with magnetism have indicated that the time for the water to return to a "normal" state can be from 1 [4] to 200 h.[2] Our measurement results for 600 W microwave irradiation suggest that it would be on the order of hours before the surface tension returned to its original value.

CONCLUSIONS

We have shown that water retains some lasting effects following microwave irradiation. The mechanism by which the interfacial layer is manipulated, resulting in a reduction in surface tension, appears to be similar to that for magnetically treated water. The effects observed in this study are for small droplets with a diameter of only a few millimeters, which is well below the limit of the microwave penetration depth of around 1.4 cm.[34] Despite the limited penetration, the phenomenon can be applied to control foam and emulsion formation and to improve chemical reactions in miniature devices.

ASSOCIATED CONTENT

Supporting Information

The modeling equations for cooling temperature are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: c.phan@curtin.edu.au.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Ikezoe, Y.; Hirota, N.; Nakagawa, J.; Kitazawa, K. Making water levitate. *Nature* **1998**, *393*, 749−750.

(2) Coey, J. M. D.; Cass, S. Magnetic water treatment. *J. Magn. Magn. Mater.* **2000**, *209*, 71−74.

(3) Yamashita, M.; Duffield, C.; Tiller, W. A. Direct Current Magnetic Field and Electromagnetic Field Effects on the pH and Oxidation−Reduction Potential Equilibration Rates of Water. 1. Purified Water. *Langmuir* **2003**, *19*, 6851−6856.

(4) Otsuka, I.; Ozeki, S. Does Magnetic Treatment of Water Change Its Properties? *J. Phys. Chem. B* **2006**, *110*, 1509−1512.

(5) Amiri, M. C.; Dadkhah, A. A. On reduction in the surface tension of water due to magnetic treatment. *Colloids Surf., A* **2006**, *278*, 252−255.

(6) Cai, R.; Yang, H.; He, J.; Zhu, W. The effects of magnetic fields on water molecular hydrogen bonds. *J. Mol. Struct.* **2009**, *938*, 15−19.

(7) Neas, E.; Collins, M. *Microwave Heating: Theoretical Concepts and Equipment Design*; American Chemical Society Professional Reference Book: Washington, DC, 1988; pp 7−32.

(8) Gittens, G. J. Variation of surface tension of water with temperature. *J. Colloid Interface Sci.* **1969**, *30*, 406−412.

(9) Vargaftik, N.; Volkov, B.; Voljak, L. *International Tables of the Surface Tension of Water*; American Chemical Society and the American Institute of Physics for the National Bureau of Standards: Washington, DC, 1983.

(10) Cini, R.; Loglio, G.; Ficalbi, A. Temperature dependence of the surface tension of water by the equilibrium ring method. *J. Colloid Interface Sci.* **1972**, *41*, 287−297.

(11) Kayser, W. V. Temperature dependence of the surface tension of water in contact with its saturated vapor. *J. Colloid Interface Sci.* **1976**, *56*, 622−627.

(12) Laurent, R.; Laporterie, A.; Dubac, J.; Berlan, J.; Lefeuvre, S.; Audhuy, M. Specific activation by microwaves: myth or reality? *J. Org. Chem.* **1992**, *57*, 7099−7102.

(13) Goncalo, P.; Roussel, C.; Marie Melot, J.; Vebrel, J. Contribution of microwaves in organic synthesis: statement of a methodology for the microwave-induced preparation of benzofuran-2(3H)-one and its comparison with classical heating. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2111−2115.

(14) Kuhnert, N. Microwave-Assisted Reactions in Organic Synthesis—Are There Any Nonthermal Microwave Effects? *Angew. Chem., Int. Ed.* **2002**, *41*, 1863−1866.

(15) Kappe, C. O. Microwave dielectric heating in synthetic organic chemistry. *Chem. Soc. Rev.* **2008**, *37*, 1127−1139.

(16) Loupy, A.; Monteux, D.; Petit, A.; Aizpurua, J. M.; Domínguez, E.; Palomo, C. Towards the rehabilitation of the Leuckart reductive amination reaction using microwave technology. *Tetrahedron Lett.* **1996**, *37*, 8177−8180.

(17) Bao, J.; Zhang, A. Poly(methyl methacrylate) nanoparticles prepared through microwave emulsion polymerization. *J. Appl. Polym. Sci.* **2004**, *93*, 2815−2820.

(18) Hoogenboom, R.; Schubert, U. S. Microwave-Assisted Polymer Synthesis: Recent Developments in a Rapidly Expanding Field of Research. *Macromol. Rapid Commun.* **2007**, *28*, 368−386.

(19) Yanagawa, H.; Kojima, K.; Ito, M.; Handa, N. Synthesis of polypeptides by microwave heating I. Formation of polypeptides during repeated hydration-dehydration cycles and their characterization. *J. Mol. Evol* **1990**, *31*, 180−186.

(20) Zhu, X.; Chen, J.; Cheng, Z.; Lu, J.; Zhu, J. Emulsion polymerization of styrene under pulsed microwave irradiation. *J. Appl. Polym. Sci.* **2003**, *89*, 28−35.

(21) Yeneneh, A. M.; Chong, S.; Sen, T. K.; Ang, H. M.; Kayaalp, A. Effect of Ultrasonic, Microwave and Combined Microwave-Ultrasonic Pretreatment of Municipal Sludge on Anaerobic Digester Performance. *Water, Air, Soil Pollut.* **2013**, *224*, 1−9.

(22) Bagnell, L.; Cablewski, T.; Strauss, C. R.; Trainor, R. W. Reactions of Allyl Phenyl Ether in High-Temperature Water with Conventional and Microwave Heating. *J. Org. Chem.* **1996**, *61*, 7355−7359.

(23) Zuo, Y. Y.; Ding, M.; Bateni, A.; Hoorfar, M.; Neumann, A. W. Improvement of interfacial tension measurement using a captive bubble in conjunction with axisymmetric drop shape analysis (ADSA). *Colloids Surf., A* **2004**, *250*, 233−246.

(24) Noordmans, J.; Busscher, H. J. The influence of droplet volume and contact angle on liquid surface tension measurements by axisymmetric drop shape analysis-profile (ADSA-P). *Colloids Surf.* **1991**, *58*, 239−249.

(25) Du, Q.; Freysz, E.; Shen, Y. R. Surface Vibrational Spectroscopic Studies of Hydrogen Bonding and Hydrophobicity. *Science* **1994**, *264*, 826−828.

(26) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, England, 1979.

(27) Wohlfarth, C. Surface tension of the mixture (1) ethanol; (2) ethane-1,2-diol. Supplement to IV/16; Springer, 2008; pp 421−422.

(28) Azizian, S.; Hemmati, M. Surface Tension of Binary Mixtures of Ethanol + Ethylene Glycol from 20 to 50 °C. *J. Chem. Eng. Data* **2003**, *48*, 662−663.

(29) Fan, Y.; Chen, X.; Yang, L.; Cremer, P. S.; Gao, Y. Q. On the Structure of Water at the Aqueous/Air Interface. *J. Phys. Chem. B* **2009**, *113*, 11672−11679.

(30) Phan, C. M.; Le, T. N.; Nguyen, C. V.; Yusa, S.-i. Modeling Adsorption of Cationic Surfactants at Air/Water Interface without Using the Gibbs Equation. *Langmuir* **2013**, *29*, 4743−4749.

(31) Park, S.; Fayer, M. D. Hydrogen bond dynamics in aqueous NaBr solutions. *Proc. Natl. Acad. Sci. U.S. A.* **2007**, *104*, 16731−16738.

(32) Ni, Y.; Gruenbaum, S. M.; Skinner, J. L. Slow hydrogen-bond switching dynamics at the water surface revealed by theoretical two-dimensional sum-frequency spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 1992−1998.

(33) Colic, M.; Morse, D. The elusive mechanism of the magnetic 'memory' of water. *Colloids Surf., A* **1999**, *154*, 167−174.

(34) Nüchter, M.; Ondruschka, B.; Bonrath, W.; Gum, A. Microwave assisted synthesis−a critical technology overview. *Green Chem.* **2004**, *6*, 128.