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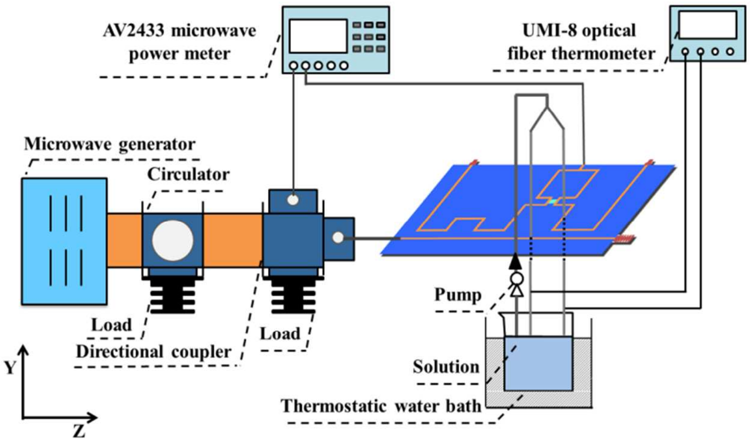

Title: The schematic of a specially designed microwave experimental system.

A sensitive experimental system to measure the dielectric properties of the polar solution under low-intensity microwave fields.

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COMMUNICATION

Experimental study of dielectric property changes in DMSO-primary alcohol mixtures under low-intensity microwave

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By applying a low-intensity microwave to DMSO-primary alcohol mixtures, distinct dielectric property changes have been observed. The results indicated that the intermolecular interaction in these mixtures could be affected by the applied electric field with the order of 10^5 V/m.

Microwave nonthermal effects are postulated to result from a proposed direct interaction of the electric field with polar molecules in the reaction medium that is not related to a bulk temperature effect. Over the past decades, nonthermal effects have been extensively studied by a number of experimental techniques and theoretical methods, but many of their aspects remain controversial. In 1996, Stuerga and Gaillard have predicted that an electric field intensity up to 10^7 V/m is required to produce a measurable microwave nonthermal effect.[1,2] Some experiments also suggested that microwave fields could disrupt the weak intermolecular bonds in proteins as well as polar solution.[3,4] Besides, investigating the changes of dielectric property induced by external electric fields (and therefore of the microwave power) is an effective approach to interpret the microwave nonthermal mechanisms. Therefore, a significant amount of published works have been devoted to this area. Theoretical works were largely conducted in a wide range of high electric fields from 10^9 V/m to 10^{11} V/m,[5-22] most of which focused on the high electric fields effects on dielectric constant change by virtue of quantum chemical calculations and molecular dynamics (MD) simulations.[9-12] However, measuring the dielectric property of solution in such high electric fields is technologically difficult, and few experimental results are available in the literature. Substantial experimental progress has been made below 10^9 V/m. In 1929, Herweg measured the relative electric permittivity (Δε) of diethyl ether, which was found to be quadratically dependent on the electric field intensity.[23] This motivated another wave of experimental studies on the relationship between the electric field intensity and the dielectric properties of material.[24-30] For example, the refractive index of water was found to change at 474THz under the 4×10^8V/m electric field.[26] Similar change was further confirmed in the wat permittivity ($\varepsilon=\varepsilon'+j\varepsilon''$) with more precise experiments based on silicon microstrip device, where it was established that ε' and ε'' changed up to 70% and 50% under a 1×10^8V/m electric field.[27] When the electric field strength decreased to 10^7V/m, Richert and co-workers investigated the nonlinear dielectric effects of propylene glycol, and it was observed that the dielectric constant decreased while the dielectric loss increased with the electric field.[28,29] Moreover, by employing high voltage frequency-domain impedance technology, more than 6% increment in the dielectric loss of glycerol was obtained when varying the external electric field from 1.4×10^6 to 2.8×10^7 V/m.[30,31] Nevertheless, little attention has been paid to solution's dielectric property changes in the presence of 10^5 V/m electric field, though 10^5 V/m is the most commonly used electric field intensity in a microwave chemistry reactor. Furthermore, an anomaly in the imaginary part of the permittivity was observed in our previous experiment report for DMSO-H_2O mixtures.[32] MD simulations also suggested that the hydrogen bonds in DMSO-primary alcohol mixtures were weaker than the sole substance of methanol and ethanol liquid.[33, 34] Therefore, DMSO-primary alcohol mixtures were chosen as the subjects of the experiment.

In this paper, we designed an experimental system to measure the dielectric behavior of DMSO-methanol/ethanol mixtures under low-intensity microwave fields (10^5V/m electric field amplitude). A specially designed microstrip sensor with high sensitivity to dielectric changes was employed to generate a uniform electric field. Then, we introduced this highly sensitive sensor into a microwave system to measure the dielectric property changes of mixtures which flowed through the designed sensor under microwave irradiation. The temperature effects caused by microwave heating were excluded by the well-designed device. measurement, slight dielectric property changes with microwave power at 2.45GHz were explored and observed. It is reasonable to infer that the intermolecular interaction in mixtures can be significantly affected by external electric field in the order of 10^5V/m.

In the precisely designed experimental apparatus, we first proposed and demonstrated a high-sensitivity radio frequency (RF)

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sensor to detect the slight dielectric property changes of solution in a flowing channel. Interference is used to cancel background probing signals to improve the sensor's sensitivity. The designed center frequency is 2.45 GHz, and a picture of the obtained sensor is shown in Fig. 1. Supposing that the solutions' dielectric properties in the two channels remain unchanged, the two signals will cancel each other. Otherwise, their difference will be measured, if the dielectric properties of solution in the material under the test (MUT) channel change.

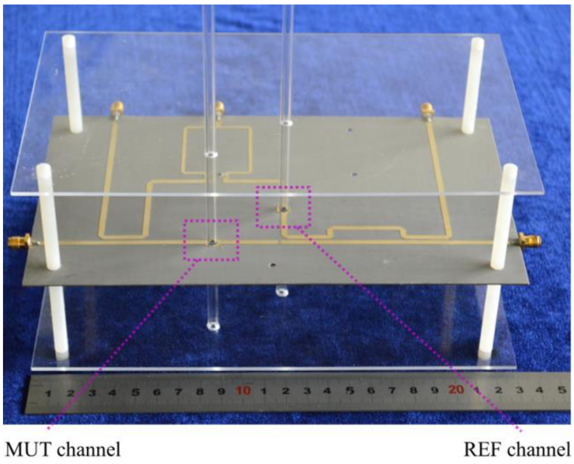

Fig. 1 Photograph of the high-sensitivity sensor.

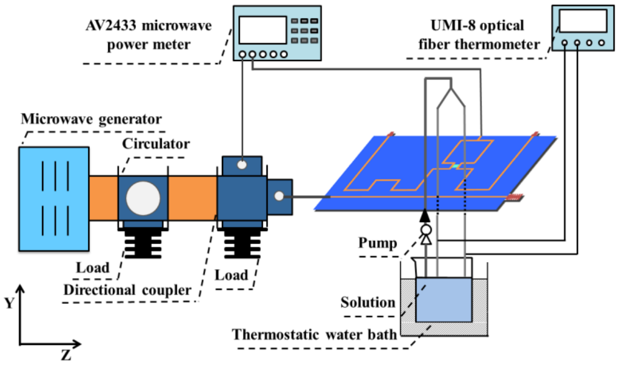

Fig. 2 The schematic of actual experimental system.

Then, the designed sensor was introduced to the following high power experimental setup, which is shown in Fig. 2. A continuous microwave source with the fixed frequency of 2.45 GHz was used to generate a stable output power. The microwaves were orderly transmitted along the circulator, the directional coupler, and eventually fed into the microstrip sensor. The Load located at the end of the microstrip sensor ensured that only a minimal amount of microwave power was reflected.

The precisely designed experiments include the following four techniques: (1) Two via holes in the microstrip rings were designed in two channels to produce a uniform distribution electric field around the solution; when the input power was up to 66 W, the electric field intensity in MUT channel reached 1.17×10^5 V/m, which was two orders of magnitude larger than that in the reference material (REF) channel. (2)Two equal parts of the measured solution were continuously pumped to the quartz glass pipelines (the diameter is 3 mm) at 8.3m/s, respectively. (3) The temperature of the solution under test was precisely controlled by using a HWCL-3 thermostat Magnetic Blenders (±0.5 C). (4) By applying the UMI-8 optical fiber probe temperature monitoring device, an accurate evaluation of the temperature difference between the output port of two pipelines located in the channels has been performed; the maximum temperature difference between them was less than 0.05°C, which guarantees us to eliminate the thermal effects caused by microwave heating.

All pure DMSO (99.5%), methanol (99.5%), and ethanol (99.5%) (analytical reagent) solutions used in these experiments were purchased from Chengdu Kelong Chemical Reagent Factory without further purification. Two sets of primary alcohol-DMSO mixtures, methanol/DMSO (methanol mole fraction 1.75, 0.58, 0.35) and ethanol/DMSO (ethanol mole fraction 1.22, 0.41, 0.24), were prepared. In our experiments, a continuous microwave source was employed, and the generator's power ranged from 20W to 100W operating at the frequency of 2.45GHz. When the input power gradually increased from 20W to 100W, the measured ratio values between output and input power were illustrated in the Cartesian coordinate system. If the ratio curves were not linear, it meant the dielectric properties of the solution in the MUT channel have changed. Each binary mixture was measured at the room temperature of 300K and repeated six times to eliminate systematic errors. The results are shown in Fig. 3 with error bars.

As illustrated in Figs. 3 (a) and (b), a similar characteristic was found in the curves of methanol-DMSO and ethanol-DMSO mixtures with different mole fraction. The output power versus input power curves were initially linear, and turned out to appear nonlinear characteristics. The curve's slope became smaller at some "critical point", which can be viewed as evidence for an electric field induced dielectric property changes in these mixtures. The "critical point" was defined as the value of input power corresponding to the point where the nonlinear characteristic first appeared. Note that all these "critical point" values are corresponding to the electric field amplitude of 10^5 V/m according to the simulated results by Ansoft High Frequency Structure Simulation (HFSS) software.

However, when the same experimental operations were performed on the sole component DMSO, methanol, and ethanol solutions, the power ratio curves were linear with the input power increasing from 20W to 100W, indicating that the dielectric properties remained unchanged for the sole substance. The results are shown in Figs 3(c) and 3(d). These measured linear results further excluded the trivial effects caused by high-power microwave (such as electromagnetic crosstalk), and proved the reliability of our experimental system. In summary, by comparing the mixture's nonlinearity with the pure substance's linearity, we can deduce that low-intensity microwave is able to affect the intermolecular interaction in DMSO-methanol/ethanol mixtures, and this microscopical interaction eventually results in the macroscopical dielectric changes in our measurements under the stimulus of a 10^5V/m electric field.

In addition, several works have demonstrated that polar mixtures of DMSO with different solvents methanol and ethanol also presented properties' deviating from ideality, such as density, viscosity, and relative permittivity.[35-38] Besides, DMSO is an aprotic polar solvent with no ability to form hydrogen bonds with another DMSO molecule.[34] Methanol tends to form chainlike hydrogen bonds in linear structure,[39] and a predominantly winding hydrogen bond chain structure is found in liquid ethanol.[40] Thus, it can be easily figured out that when DMSO solvent is dissolved into the methanol/ethanol solution, the hydrogen-bond interaction leads to a structural reorganization compared with their pure components. In other words, when DMSO is added, the long chainlike hydrogen bonds of methanol and ethanol liquid transform into dimers or trimers in mixtures with less hydrogen-bond numbers.[41]

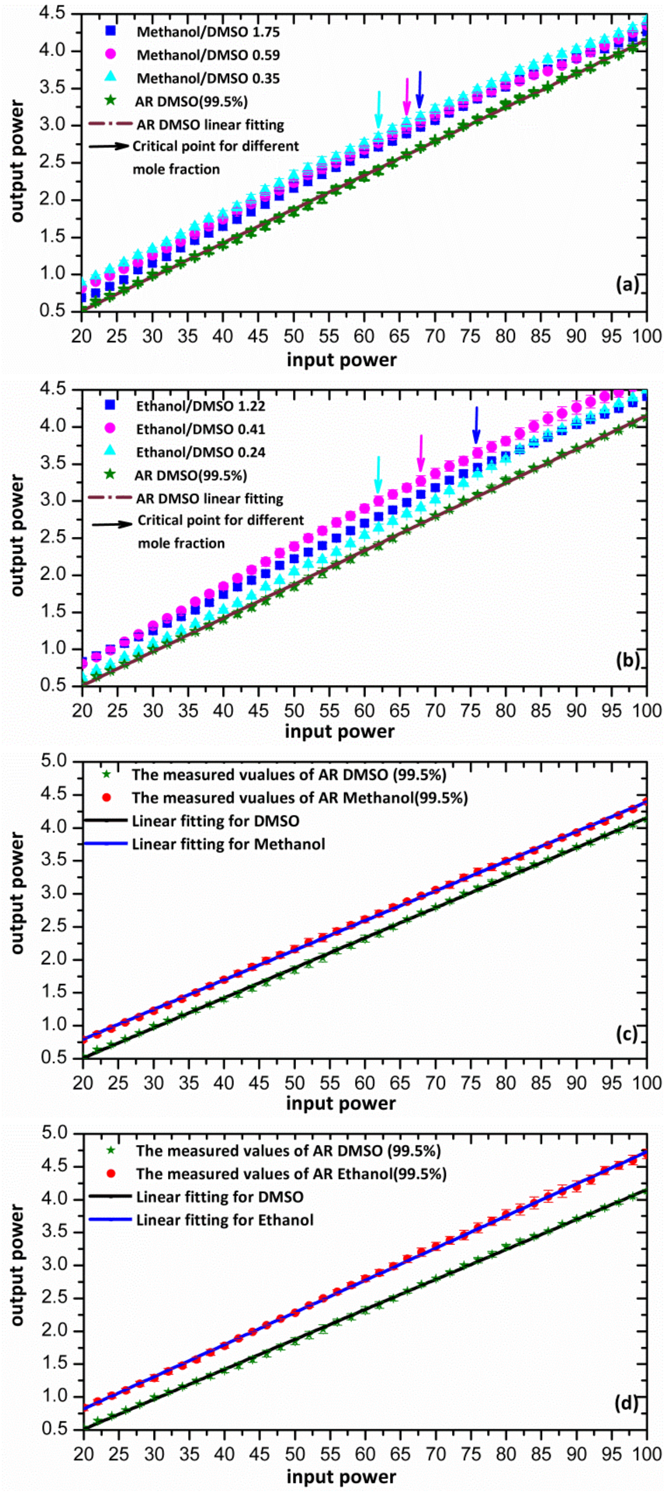

Fig. 3 The relationships of output-input microwave power for solutions with different mole fraction ratios: (a) methanol/DMSO mixtures at methanol mole fraction of 1.75, 0.58, 0.35, (b) ethanol/DMSO mixtures at ethanol mole fraction of 1.22, 0.41, 0.24, (c) pure DMSO (99.5%) and methanol(99.5%) solution, (d) pure DMSO and ethanol(99.5%) solution.

As a result, these weak hydrogen bonds are supposed to be altered under a low-intensity microwave in our experiment. And recently experiments on heat-shock proteins (HSPs) have suggested that low-intensity microwave could disrupt the weak bonds that maintain the active folded forms of proteins.[4]

Conclusions

In summary, we have proposed a sensitive microwave experimental system which can detect the dielectric property changes of DMSO-methanol/ethanol mixtures under low-intensity microwave fields. In our experiments, the corresponding electric field is 10^5 V/m. The conclusions are summarized as follows: (1) The measured linear results of sole component verified the reliability of our experimental system; (2) In the presence of a 10^5V/m electric field, the measured results indicated that the dielectric properties changed in mixtures while no change was observed in their pure substance; (3) Based on the experimental results, it can be deduced that the application of low-intensity microwave can affect and alter the intermolecular interaction in DMSO-methanol/ethanol systems, thereby leading to macroscopical dielectric property changes in mixtures. The results validate the existence of a nonthermal microwave effect in low-level intensity electric fields. Further theoretical work on the details of interaction mechanism between microwave and mixtures is currently underway in our laboratory.

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