

Measurement/Computation of Effective Permittivity of Dilute Solution in Saponification Reaction

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Abstract—For better application of microwaves in chemistry, the interaction between the microwave and chemical reaction needs to be further studied. Since the reactants form a complicated mixture, which changes with time, an effective permittivity can be used to describe the molecular polarization of the mixture in the reaction. The effective permittivity is expected to change with the frequency of the microwave, temperature, and reaction time. However, in many cases, change of the effective permittivity in saponification reaction is too small to be detected using traditional methods. In this paper, we present a hybrid experimental/computational method for determining the effective permittivity in saponification reaction. First, we use a resonant coaxial sensor to measure the reflection coefficients. To predict its performance, the electromagnetic-field distribution near the sensor and the reflection coefficient are calculated employing the frequency-dependent finite-difference time-domain method. Second, we develop a genetic-algorithm-based inverse-calculation technique and employ it to determine the complex permittivity of pure water from the measured reflection coefficient and compare the results with that obtained from Debye's equation. Finally, the hybrid experimental/computational method is employed to determine the effective permittivity of a dilute solution in a typical saponification reaction. Results are presented and discussed.

Index Terms—Effective permittivity, inverse calculation, measurement, saponification reaction.

I. INTRODUCTION

IN THE EARLY 1980s, microwaves were proposed to be used for accelerating chemical reactions by their efficient heating of the reactants. This technique was validated later on by experiments, and since then, microwaves have been widely used in chemistry [1]. Unfortunately, however, some difficulties arose in the application of high-power microwaves in chemistry, which limited the transfer of the laboratory experiment system to industrial applications. Two of the main problems are as follows.

- The reflection and absorption of a microwave by the reactants change nonlinearly with time during the reaction [2]. When high-power microwaves are applied, the rapid increment of reflection and absorption may destroy the microwave generator and may burn the organic reactants, which is a similar phenomenon such as the

dielectric breakdown that may happen in the application of microwaves in dielectric heating [3].

- It is very difficult to get a uniform microwave heating of the reactants.

To overcome these difficulties, the interaction between microwaves and the chemical reaction needs to be further studied. Since the reactants form a complicated mixture, which changes with time, an “effective permittivity” can be used to describe the molecule polarization of the mixture during the reaction procedure. The effective permittivity is expected to change with the frequency of microwaves, temperature, and reaction time.

As a very useful reaction, the saponification reaction has been carefully studied [4]. However, in most cases, the effective permittivity change in the dilute solution during the saponification reaction is too small to be observed using traditional methods due to the high dielectric constant of water. In this paper, we present a hybrid experimental/computational method for determining the “effective permittivity” in the saponification reaction. First, we use a new resonant structure of a coaxial line to measure the reflection coefficients. To predict the performance of the resonant coaxial structure, the electromagnetic-field distribution near the sensor and the reflection coefficients at different frequencies are calculated. In the calculation, a frequency-dependent finite-difference time-domain (FDTD) method [5] is employed because the dilute solution to be studied is a dispersive material. Second, we develop a genetic-algorithm (GA)-based inverse-calculation technique and employ it to determine the complex permittivity of pure water from the measured reflection coefficient and compare the results with that obtained from Debye's equation. Finally, the hybrid experimental/computational method is employed to determine the effective permittivity of the dilute solution in a typical saponification reaction. The experimental/computational results show that the coaxial sensor is very sensitive to the change of the effective permittivity with time near the resonant frequency.

II. STRUCTURE OF THE COAXIAL SENSOR AND THE MEASUREMENT APPARATUS

Many structures using coaxial lines have been reported for measuring the permittivity of a solution or powder [6], [7]. However, as mentioned above, in many cases, a change of the effective permittivity in the saponification reaction is too small to be observed by using traditional methods. In this paper, we propose a resonant structure using a slotted open-ended coaxial line. The slotted open-ended coaxial line works as a cavity loaded by the

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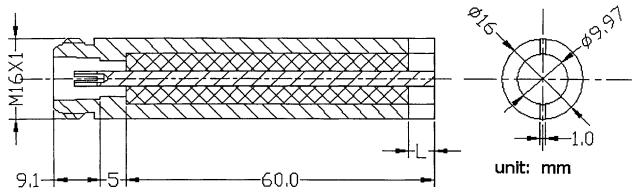


Fig. 1. Structure of the coaxial sensor.

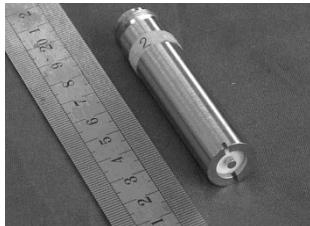


Fig. 2. Coaxial sensor.

solution under test to measure the reflection coefficient, which is sensitive to small changes of the effective permittivity of the solution in the cavity. The slot is made for pushing air bubbles out of the cavity when the sensor is immersed in the solution. This is necessary because the air bubbles may significantly affect the accuracy of the measurement. The width of the slot has to be chosen correctly to push the air bubbles out easily and, meanwhile, to avoid too much emission of electromagnetic energy to maintain a significant resonance. Since most of the solutions are highly corrosive in chemical experiments, the whole structure is gold plated. The structure of the sensor and the sensor itself is illustrated in Figs. 1 and 2, respectively. Six sensors have been made and used in the experiments with different cavity lengths $L = 2, 4, 5, 6, 8$, and 10 mm in order to achieve different resonant frequencies.

The measurement apparatus using the coaxial sensor is shown in Fig. 3. A beaker of 20-cm diameter containing the solution is immersed in a water bath to keep the temperature constant. Two sensors are used for the measurements in order to get enough data. They are fixed by two clamp stands and they are separated far from each other and from the wall of the beaker. The reflection from the beaker wall and the mutual influence between the sensors can be ignored due to the fast decay of the electromagnetic field in the solution. The Wiltron Vector Network Analyzer 3734A is used to measure the reflection coefficients and the data are sampled per 15 s.

III. COMPUTATION OF THE FIELD DISTRIBUTION AND REFLECTION COEFFICIENT

To predict the performance of the proposed resonant coaxial sensor, in this section, we study the electromagnetic-field distribution near the cavity and the reflection coefficient when the sensor is immersed in pure water. First, we employ the FDTD to compute the fields near the cavity. The computational region is discretized by Yee's grid, and the components of the electric and magnetic fields in the cylindrical coordinate system are given in

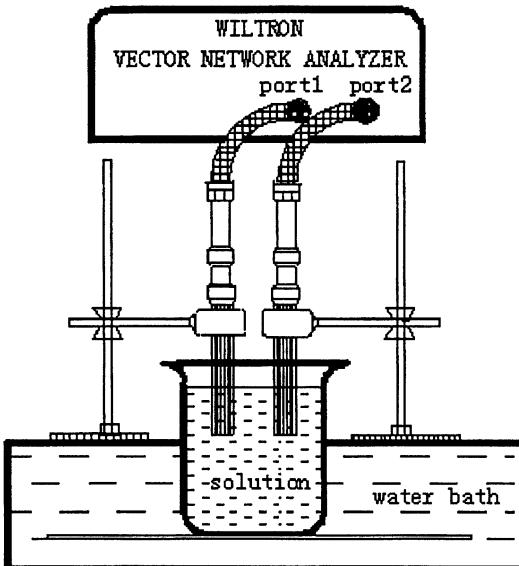


Fig. 3. Measurement apparatus.

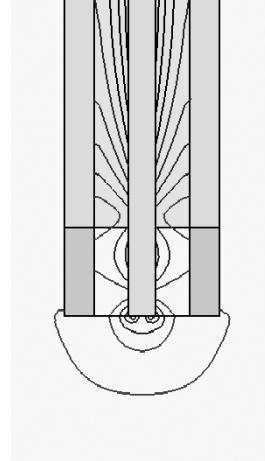


Fig. 4. Distribution of total electric field near the end of the sensor.

[8] and [9] and, hence, are not repeated here. In the calculation, the space and time increments are selected to be

$$\begin{aligned}\Delta t &= 0.208 \times 10^{-13} \text{ s} \\ \Delta r &= 0.5 \text{ mm} \\ \Delta\varphi &= 0.1047 \text{ rad} \\ \Delta z &= 0.5 \text{ mm.}\end{aligned}\quad (1)$$

From the computational results, distributions of the total electric and magnetic fields at 2.45 GHz are plotted in Figs. 4 and 5. The results illustrated in these figures show that the fields concentrate near the end of the sensor. This feature can avoid environmental interference and ensure an accurate measurement.

From the computational results of the electromagnetic fields, the reflection coefficients are also determined and then compared with the measurement data at various frequencies. Corresponding to different frequencies, the complex permittivity of pure water, needed for the forward computation of the reflection coefficient, is also different, and its values are determined by using the formulas given in [9] and [10]. The

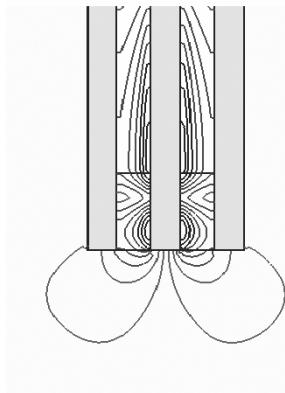


Fig. 5. Distribution of total magnetic field near the end of the sensor.

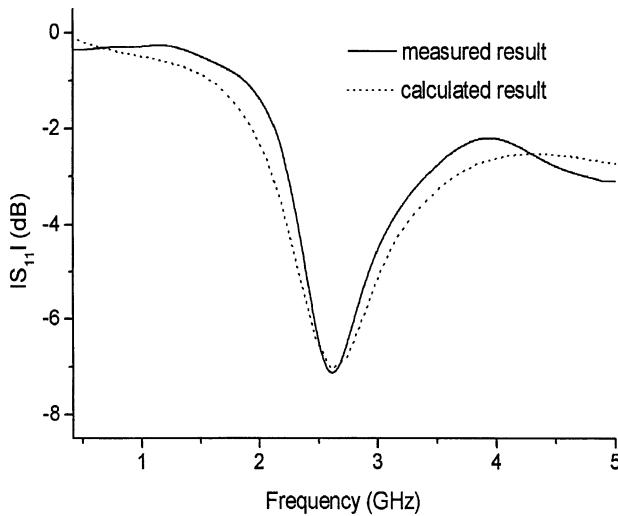


Fig. 6. Measured and calculated magnitude of the reflection coefficient at 26 °C.

comparisons of the calculated and measured magnitude of the reflection coefficient at various frequencies are shown in Figs. 6 and 7, in which a good agreement is observed. In addition, from these two figures, we see that the resonant frequency is higher at a higher temperature.

IV. INVERSE CALCULATION

From the measured reflection coefficient, the effective permittivity of the solution of interest can be calculated. Unlike the previously published research, which used some calibrated parameters to calculate the effective permittivity, in this paper, we employ an inverse-calculation method, based on an improved GA, to reconstruct the permittivity of the solution. To validate the inverse-calculation method, in this section, we use it to determine the complex permittivity of pure water and then compare the results with that obtained from Debye's equation [10].

As the first step of the inverse calculation, a set of reflection coefficients is obtained by forward calculation employing the FDTD method from a set of randomly initiated complex permittivity. The set of complex permittivity constructs the initial population of the potential solutions and the reflection coeffi-

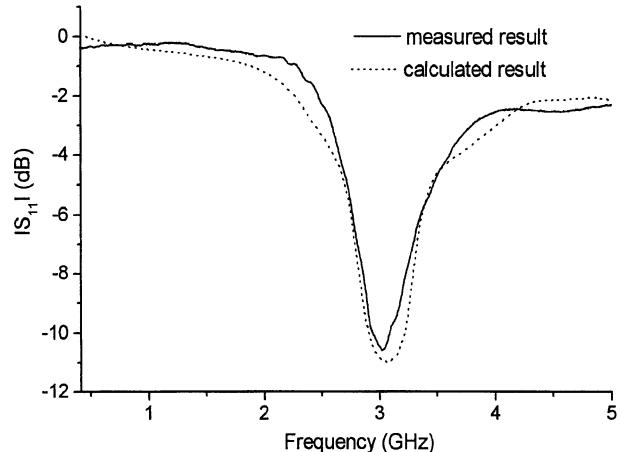


Fig. 7. Measured and calculated magnitude of the reflection coefficient at 80 °C.

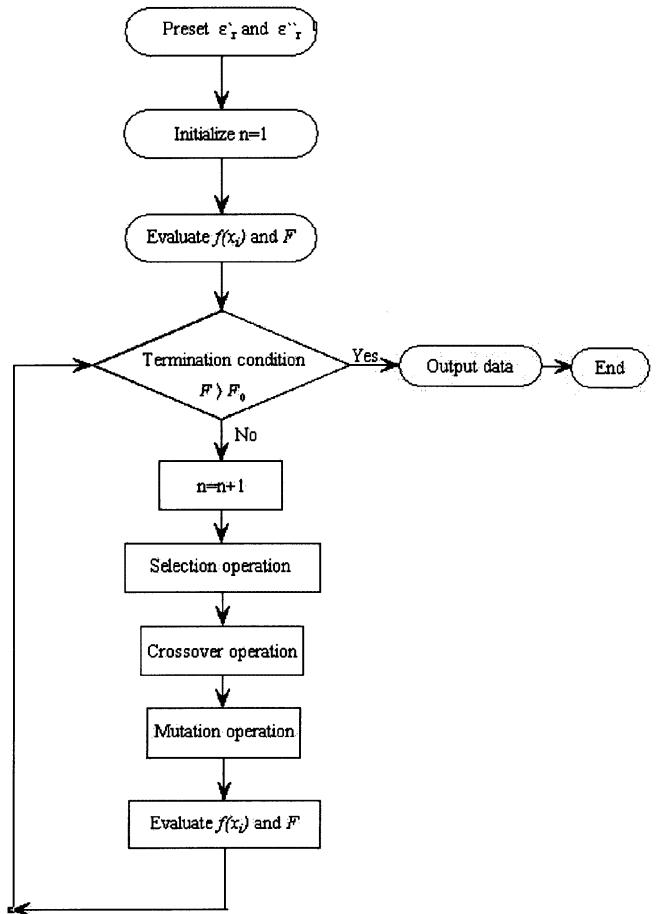


Fig. 8. Inverse-calculation procedure.

cients are transformed into the objective values by the objective function defined by

$$f(x_i) = \left[\alpha_1 (|S_{11c}| - |S_{11m}|)^2 + \alpha_2 (\theta_c - \theta_m)^2 \right]^{(1/2)} \quad (2)$$

where $|S_{11c}|$ and θ_c are the magnitude and phase of a set of the calculated reflection coefficients, $|S_{11m}|$ and θ_m are the amplitude and phase of the measured reflection coefficients, and

TABLE I
COMPARISON OF THE COMPLEX PERMITTIVITY OBTAINED BY GA
WITH THAT BY DEBYE'S EQUATION

	40°C		50°C		60°C		70°C		80°C	
	ϵ_{eff}^r	ϵ_{eff}^i								
GA result	70.72	5.63	69.02	4.85	66.07	3.37	61.87	2.97	59.38	2.22
Debye's result	71.63	6.02	68.34	4.63	65.28	3.61	62.44	2.85	59.82	2.28
Relative errors	-1.3%	-6.9%	1.0%	4.5%	1.2%	-7.1%	-0.9%	4.0%	-0.7%	-2.7%

α_i ($i = 1, 2$) is the weight factor. In our computation, α_i is taken to be $\alpha_1 = 0.9$ and $\alpha_2 = 0.15$. The objective values are then mapped into fitness values by the fitness function defined by

$$F = \exp [-\alpha_0 f(x_i)] \quad (3)$$

where α_0 is an empirical parameter, and is taken to be 0.33 in our calculation. In order to select better and better individuals in the population, some special techniques, such as stochastic universal sampling (SUS) [11] and the elitist strategy [12], are employed. The evolution of survival of fitness terminates under the conditions that the fitness value is larger than a preset threshold F_0 . A block diagram of the GA-based inverse calculation is illustrated in Fig. 8.

The computation of the complex permittivity can be completed in approximately 70 min using a personal computer (PC) with 1.2-GHz CPU. The computational results of the complex permittivity determined by GA optimization are compared with that obtained from Debye's equation [10] at a frequency of 2450 MHz. The comparison is listed in Table I, and a reasonably good agreement is observed.

V. RESULTS AND DISCUSSION

Making use of the coaxial sensor and the measurement apparatus presented in Section II, the reflection coefficient of the dilute solution in a saponification reaction can be measured. From the measured reflection coefficient, the effective permittivity of the solution is then calculated by employing a GA-based inverse-calculation method described in the Section IV. A typical saponification reaction with $\text{CH}_3\text{COOC}_2\text{H}_5$ and NaOH in dilute solution is selected for the study presented in this paper. Its reaction equation is [4]



Results of the measured reflection coefficient and the calculated effective permittivity are then presented and discussed in this section.

The measurement results of the magnitude of the reflection coefficients at various frequencies for the solution at 40 °C with an initial concentration of the reactant $C_0 = 0.2 \text{ mol/l}$ and $C_0 = 0.1 \text{ mol/l}$ are shown in Figs. 9 and 10, respectively. Data are collected every 15 s, but only a few curves representing sample data are plotted in each of these two figures. The curves illustrate

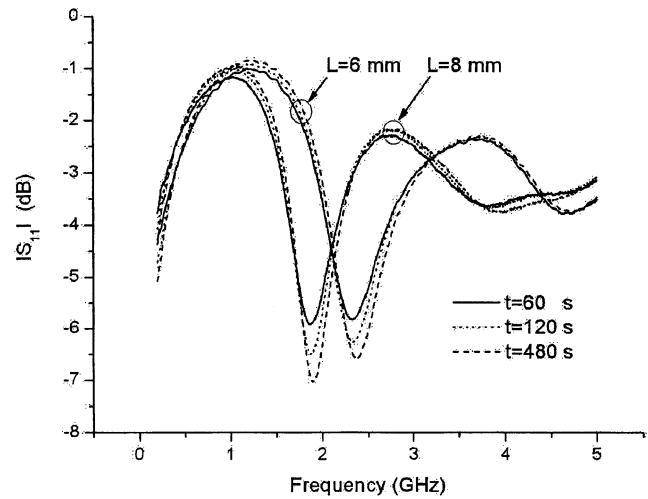


Fig. 9. Magnitude of the reflection coefficient versus frequency and time for $C_0 = 0.2 \text{ mol/l}$.

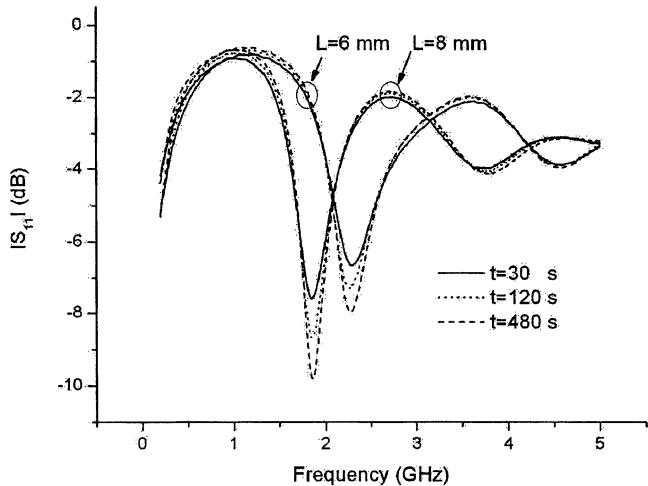


Fig. 10. Magnitude of the reflection coefficient versus frequency and time for $C_0 = 0.1 \text{ mol/l}$.

how the reflection coefficient changes as the time progresses, which corresponds to the change of the effective permittivity of the solution during the saponification reaction. We observe from these two figures that the coaxial sensor is very sensitive near the resonant frequency, and the sensor with a shorter cavity

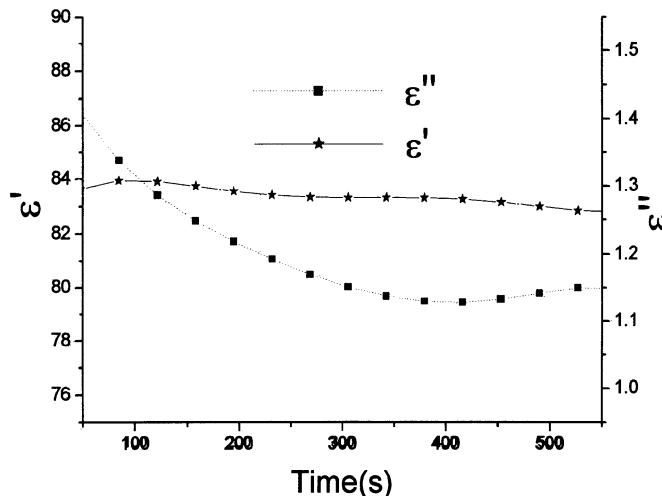


Fig. 11. Effective permittivity of the solution at 25 °C.

length L has a higher resonant frequency. Hence, the resonant frequency could be changed by varying the cavity length L to trace the permittivity change at a desire frequency. Also, we see that the curves in the vicinity of the resonant frequency become sharper in Fig. 10 comparing with that in Fig. 9 because the solution with a smaller initial concentration of the reactant has a lower conductivity.

From the measured reflection coefficient, the unknown effective permittivity of the dilute solution in the saponification reaction can be calculated employing the GA-based inverse-calculation technique described in the previous section. The results of the calculated effective permittivity are shown in Fig. 11. From this figure, we observe that during the saponification reaction, the real part of the effective permittivity of the dilute solution remains almost constant, but its imaginary part changes significantly due to the significant change of the conductivity of the solution. In fact, the significant change of the conductivity could be used to determine the reaction rate [4].

VI. CONCLUSION

In this paper, we have presented a hybrid experimental/computational method for determining the effective permittivity of a dilute solution in a saponification reaction. First, a new resonant structure of a coaxial line has been used to measure the reflection coefficient of the dilute solution. To predict the performance of the resonant coaxial structure, we calculated the electromagnetic-field distribution near the coaxial sensor and the reflection coefficient employing the frequency-dependent FDTD method when the sensor is immersed in pure water. It has been found that the fields concentrate near the end of the sensor. A comparison between the computed reflection coefficient and measurement results has also shown that they agree with each other. Second, we have developed a GA-based inverse-calculation technique and employed it to determine the complex permittivity of pure water from the measured reflection coefficient. The computational results were compared with that obtained from Debye's equation and a reasonably good agreement has been observed. Finally, the hybrid experimental/computational technique has been employed to determine the effective permittivity of a dilute solution in a typical saponification reaction. The results illustrate that the

coaxial sensor is very sensitive to the change of the effective permittivity with time near the resonant frequency, and the resonant frequency varies as the cavity length changes. The results also show that the real part of the effective permittivity of the mixture is almost unchanged, but its imaginary part changes significantly as time progresses during the reaction.

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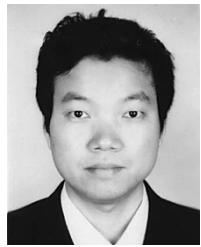
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