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A METHOD FOR CALCULATING THE EFFECTIVE PERMITTIVITY OF A MIXTURE SOLUTION DURING A CHEMICAL REACTION BY EXPERIMENTAL RESULTS

K. Huang and X. Yang

College of Electronics and Information Engineering
Sichuan University
Chengdu 610064, China

Abstract—Usually, an effective permittivity can be used to describe the molecular polarization of a mixture during a chemical reaction and consequently be used to calculate the transmission and absorption of microwave in the mixture. In this paper, we propose a method to calculate the effective permittivity of a mixture solution during a chemical reaction by means of the experimental results. To verify this method, the acetone iodination reaction is employed. The calculated effective permittivities of the mixture are in good agreement with the measured results.

1. INTRODUCTION

Currently, microwaves are widely used in chemical industry to accelerate chemical reactions [1, 2]. Unfortunately, some difficulties arose in the application of microwave energy in chemistry. For examples, thermal runaway, hot spot and explosion usually occur during microwave heating on chemical reactions [3]. Because effective permittivity can be used to describe the transmission and absorption of microwave in the mixture during a chemical reaction, to overcome the above difficulties, the effective permittivity of a mixture during a chemical reaction needs to be carefully studied. Up to now, some efficient numerical approaches have been used to study the microwave heating on water and food [4]. However, microwave heating on chemical reactions is scarcely reported due to the lack of calculation of the effective permittivity of a mixture during a chemical reaction.

In this paper, we focus on the calculation of the effective permittivity of a mixture solution during a chemical reaction. The mixture solution comprises all the chemical components and the concentration of each chemical component is anticipated to change with time and temperature. Generally, it is difficult to give an analytic expression of the effective permittivity with both variables. Here, we propose a method to calculate the effective permittivity by means of experimental results. First, we performed the reaction under three different constant temperatures and measured the effective permittivity with time at each constant temperature. Then, the three measured curves of effective permittivity with time were used to get a new curve at any constant temperature by interpolation or extrapolation. In the interpolation or extrapolation, we have to determine the corresponding moment at each curve when the mixture solutions have the same concentrations of the components according to the reaction rate. Finally, for the reaction carried out under any constant temperature, the effective permittivity of the mixture solution can be calculated at any time. Moreover, the effective permittivity of the mixture solution during the chemical reaction that carried out under a programmed-temperature can also be calculated.

To verify this method, a special acetone iodination reaction was employed under the constant temperature and programmed-temperature. The calculated results are in good agreement with the measured results.

2. THE METHOD TO CALCULATE THE EFFECTIVE PERMITTIVITY

According to the Clausius-Mossoti's and the Onsager's equations, the temperature coefficient of permittivity for polar solution is reciprocal to the temperature [5, 6]. However, for the mixture solution during a chemical reaction, we suppose the temperature coefficient of the effective permittivity is the complicated function of the reciprocal of temperature.

$$\frac{1}{\varepsilon_{\mathit{eff}}} \cdot \frac{d\varepsilon_{\mathit{eff}}}{dT} = f\left(\frac{1}{T}\right) \tag{1}$$

where, the complicated function $f(\frac{1}{T})$ should be continuous function; T is temperature; $\varepsilon_{\mathit{eff}}$ is effective permittivity. When we expand $f(\frac{1}{T})$ into the Maclaurin series [7] and neglect the high-order terms, we can get the following equation from Equation (1):

$$\frac{1}{\varepsilon_{\mathit{eff}}} \cdot \frac{d\varepsilon_{\mathit{eff}}}{dT} = -\alpha \cdot \frac{1}{T} - \delta \tag{2}$$

where α and δ are constants, they can be determined by experiment.

In order to calculate α and δ, we rewrite the Equation (2) as follows:

$$Ln\left(\varepsilon_{\mathit{eff}}^{T}/\varepsilon_{\mathit{eff}}^{T_0}\right) = Ln\,(T/T_0)^{-\alpha} - \delta(T - T_0) \tag{3}$$

where, $\varepsilon_{\mathit{eff}}^{T_0}$ is the effective permittivity of the solution under the temperature T_0; $\varepsilon_{\mathit{eff}}^{T}$ is the effective permittivity of the solution under the temperature T.

If the chemical reactions in solutions under the temperatures T_0 and T have the same components, it can be considered as the different temperature states of a same virtual mixture. So, the effective permittivity of a mixture solution under the different temperature states should satisfy the equation (3). Therefore, it is easy to see that the constant of α and δ can be calculated from Equation (3) by those previously measured under the different temperatures.

The problem is how to determine the moment of t_1 and t_2 with the same state. According to the assumption that the solutions under the temperatures T_1 and T_2 have the same components, we can obtain the following relationship:

$$K_1 t_1 = K_2 t_2 \tag{4}$$

where K_1 and K_2 are the reaction rate constant under the temperatures T_1 and T_2, respectively. They can be found in reference [8].

Once we have gotten the constants α and δ, from Equation (3), the effective permittivity can be calculated easily under the different constant temperatures.

However, the practical temperature rise of chemical reaction in solution under the microwave radiation is not usually constant. In order to determine the moment of t_1 and t_2 with the same concentrations of chemical components, we must rewrite equation (4) as follows:

$$\int_0^{t_2} K dt = K_1 t_1 \tag{5}$$

where K is the reaction rate constant varying with the temperature rise, which can be expressed as

$$K = k_0 \cdot e^{-\frac{E}{RT}} \tag{6}$$

where k_0 is the pre-exponential factor of the reaction; E is the activation energy; R is gas constant; and T is reaction temperature.

Thus, when the temperature rise curve of T versus t is given, that is, function $T(t)$ is known, the Equation (5) can be further expressed by

$$\int_0^{t_2} k_0 \cdot e^{-\frac{E}{RT(t)}} dt = K_1 t_1 \tag{7}$$

Form equations (7) and (3), the effective permittivity of a mixture solution during a chemical reaction can also be calculated easily under the temperature of $T(t)$.

3. EXPERIMENT AND RESULTS

In our experiment, a microwave vector network analyzer of Agilent E8362B was used to measure the reflection coefficients from a special designed coaxial line probe, which is merged in the solution [9]. The measurement was carried out from 400 MHz to 4 GHz. The height and diameter of the beaker must be larger than five wavelengths to get accurate results. KXS — A trough was used to control the temperature of solution in beaker. UMI-8 optical fiber thermometer with diameter of 1 mm was employed to measure the temperature of the mixture solution and a PC was used to record the temperature rise. The figure of experiment systems is shown in Fig. 1. Acetone iodination reaction is a carefully studied chemical reaction; it is widely used to study the chemical kinetics [10]. In our previously published paper, it has been observed that the significant effective permittivity changes with time during the reaction. The reaction equation is written as follows:

$$\begin{aligned} &\mathrm{KIO_3 + 5KI + 6HCl + 3CH_3COCH_3} \\ &\xrightarrow{k} \mathrm{3CH_3COCH_2I + 6KCl + 3HI + 3H_2O} \end{aligned} \tag{8}$$

The initial concentrations are $C_{\mathrm{KIO_3}} = 0.005\,\mathrm{mol/L}$, $C_{\mathrm{KI}} = 0.025\,\mathrm{mol/L}$, $C_{\mathrm{HCl}} = 1.5\,\mathrm{mol/L}$ and $C_{\mathrm{CH_3COCH_3}} = 1.5\,\mathrm{mol/L}$. The

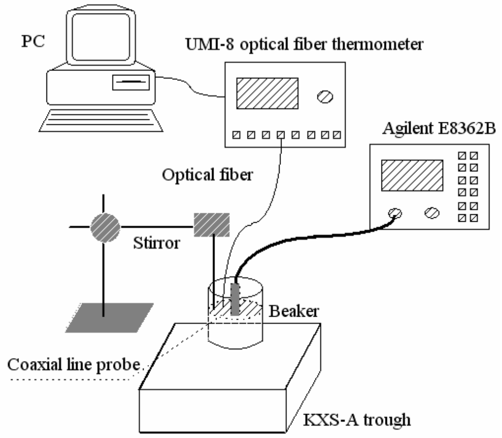


Figure 1. Experimental system.

reaction was performed under four constant temperatures (30°C, 37°C, 44°C, 52°C) and the programmed-heating condition by water bath. The temperature rise curve of programmed-heating is shown in Fig. 2.

In our experiment, the reflection coefficients were sampled per *15 seconds* automatically. These reflection coefficients can be employed to calculate the effective permittivity of the solution by means of genetic algorithms [9]. At last, the effective permittivity under the four constant temperatures and the programmed-heating condition can be obtained by measurement. The results are shown in Fig. 3–Fig. 4.

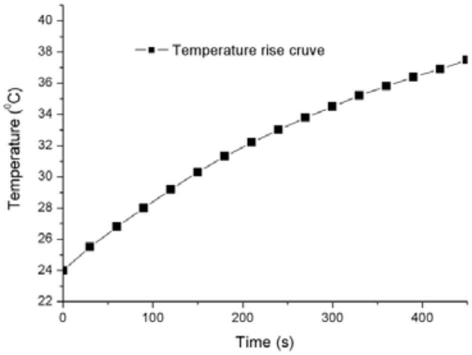
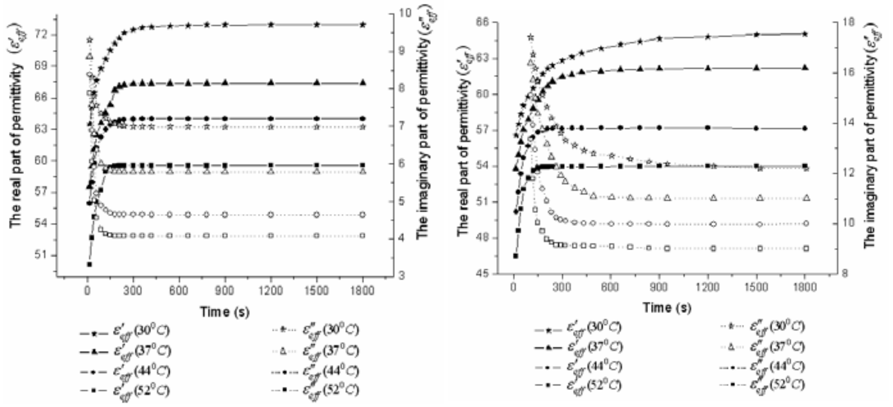


Figure 2. The programmed-temperature rise curve of acetone iodination reaction.



(a) 915MHz (b) 2450MHz

Figure 3. The real and imaginary part of effective permittivity as a function of time under four constant temperatures.

By means of the measured results in Fig. 3, the effective permittivities of three curves are used to calculate the effective permittivity of the fourth curve and compared with the measured results. There are two cases in the calculation.

(1) By using the three measured results at different constant temperatures, the effective permittivity at the intervenient temperature can be determined as above. Fig. 5 shows the comparison of the calculated and measured effective permittivities at 915 MHz and 2450 MHz. From the comparison, it is observed that the results are both in good agreement.

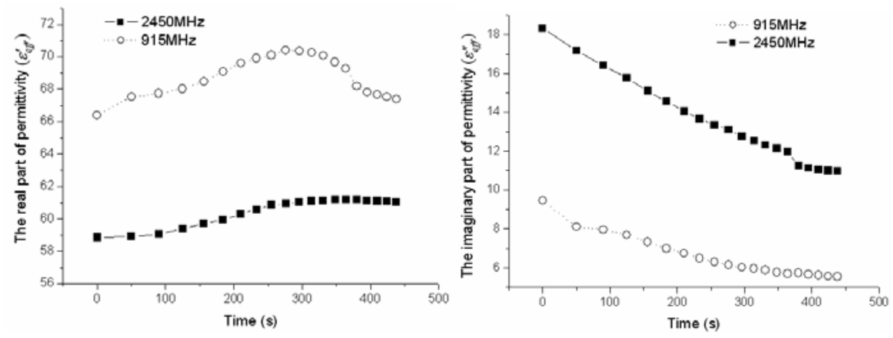
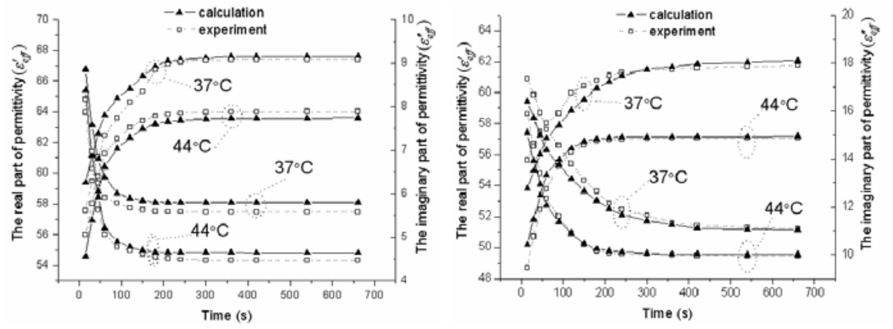


Figure 4. The real and imaginary part of effective permittivity as a function of time under the programmed-heating condition.



(a) 915MHz (b) 2450MHz

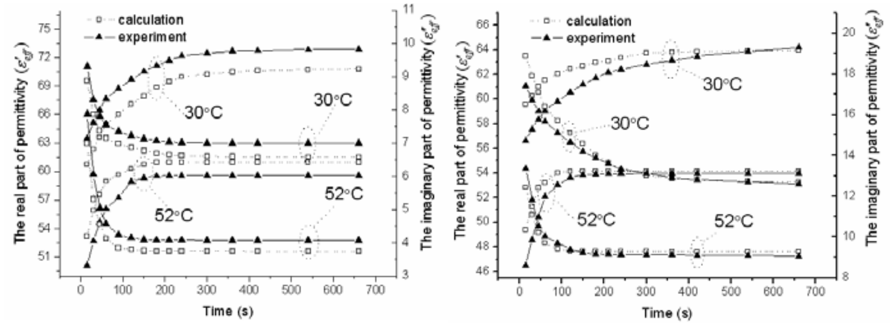
Figure 5. The comparison of the calculated and measured effective permittivity.

(2) In a similar manner, we can calculate the effective permittivity at higher or lower temperature by using the three measured results at different constant temperature. Fig. 6 shows the comparison of the

calculated and measured effective permittivities. It should be noted that the calculated results at the intervenient temperature are better than those at higher or lower temperature.

The comparison of calculated and measured results from Figs. 5–6 clearly verifies the validity of the method proposed in this paper. Nevertheless, if we use the measured effective permittivity to calculate the values at higher or lower temperature, the error could be larger.

At last, we calculate the complex effective permittivity under the programmed-heating condition by means of the measured results in Figs. 3–4 and the comparison of calculated and measured results are shown in Fig. 7.



(a) 915MHz (b) 2450MHz

Figure 6. The comparison of the calculated and measured effective permittivity.

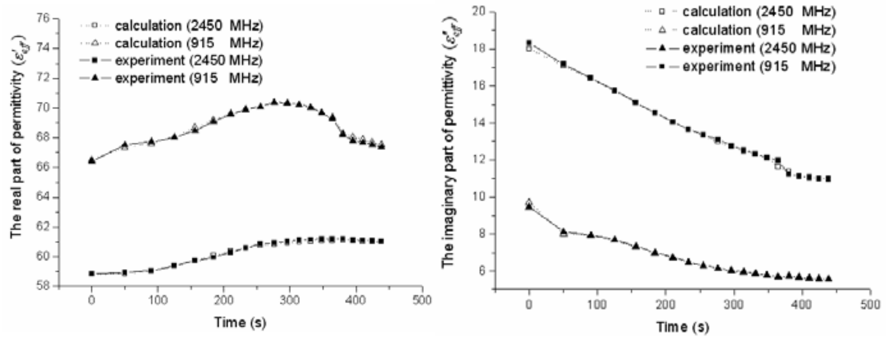


Figure 7. The comparison of the calculated and measured effective permittivity under the programmed-heating condition.

Figure 7 shows the comparison of the calculated and measured effective permittivities under the programmed-heating condition. From the comparison, it is observed that both results are in good agreement.

4. CONCLUSION

Microwave heating on chemical reactions has shown favorable application value and developing prospect. The calculation of effective permittivity is the most important preliminary work to analyse microwave heating on chemical reactions. This paper has presented a method to calculate the effective permittivity of a mixture solution during a chemical reaction. The effective permittivity of the mixture solution during acetone iodination reaction has been obtained and compared with the measured results. Good agreement between the calculated and measured results has verified the feasibility of numerical method. The method proposed here makes it possible to analyse the microwave heating on chemical reactions in solution.

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