Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5703-5710

Calculation of Effective Permittivity of Mixtures During the Microwave Heating on the Chemical Reaction

XIAO-QING YANG, KA-MA HUANG* and LI-JUN YANG
College of Electronics and Information Engineering,
Sichuan University, Chengdu 610064, P.R. China
Fax: (86)(28)85408779; Tel: (86)(28)85408779
E-mail: ljyang320@163.com

For better application of microwaves heating in chemistry, the interaction between microwave and the chemical reactions needs for further studies. Usually, an effective permittivity can be used to describe the molecular polarization of the mixture in the reaction and consequently be used to calculate the transmission and absorption of microwave in the reaction mixtures. However, there is still a lack of the calculation method for the effective permittivity of mixtures under the microwave heating on the chemical reaction. Here, a simple method based on experimental results was employed to calculate the effective permittivity of mixture during the microwave heating on chemical reaction. To corroborate this method, two chemical reactions were employed. The calculated results of effective permittivity of the mixtures are in good agreement with the measured results. Using this method, the permittivity of reaction mixture decided by temperature and its composition can be obtained.

Key Words: Effective permittivity, Microwave heating, Chemical reaction.

INTRODUCTION

Most of the chemical reactions are sensitive to temperature. Therefore using microwaves to heat chemical reactions presents an impressive application prospect. In the early 1980's, microwaves were proposed to be used for speeding up chemical reactions. Later, this technique was validated by experiments and since then microwaves have been widely used in chemistry[1]. However, some difficulties arose in the application of high-power microwaves in chemistry, which limited the transfer of laboratory experimental systems to industrial applications. Two of the main problems are the follows: (1) The reflection and absorption of microwave by the reactants change nonlinearly with time during the reaction. Sometimes, the rapidly increment of reflection and absorption may destroy the microwave generator and may burn the organic reactants when high-power microwaves are applied; (2) It is very difficult to get a uniform microwave heating of the reactants[2,3]. For better application of microwaves in chemistry, the interaction between microwave and the chemical reaction needs to be further studied. Since the reactants form a complicated mixture, which

changes with time and temperature, an effective permittivity can be used to describe the molecular polarization of the mixture in the reaction. Obviously, the effective permittivity is expected to be a function of the frequency of microwave, the temperature and the composition of reaction mixtures. Unfortunately, it is difficult to give an analytical expression of the effective permittivity for chemical reaction with composition and temperature at certain frequency. Furthermore, a number of efficient numerical approaches have been used to study the microwave heating on water and food[4]. However, for the chemical reactions, there is not a simulation method for the microwave heating process due to a lack of the calculation method for the effective permittivity of mixtures during the microwave heating on the chemical reaction.

To solve problem, in this study, a simple method based on experimental results was employed to calculate the effective permittivity of mixture during the microwave heating on chemical reaction. Because the chemical reactants change with not only with temperatures, but also the reaction time during the microwave heating. The basic assumption is to consider the reactant to be virtual mixture and its effective permittivity is decided only by its composition and temperature. For this virtual mixture, there are many rough models can be used to calculate the effective permittivity[5]. But these models are always difficult to obtain the accurate results. Instead of using these approximate models to calculate the effective permittivity, we propose a simple method based on experimental results was employed to calculate the effective permittivity of mixture during the microwave heating on chemical reaction. To corroborate this method, two chemical reactions were employed. The calculated results of effective permittivity of the mixtures are in good agreement with the measured results. Using this method, the permittivity of reaction mixture decided by temperature and its composition can be obtained.

The method to calculate the effective permittivity according to Clausius-Mossoti's and Onsager's equations, the temperature coefficient of permittivity for polarizable solution is reciprocal to the temperature[5]. However, for the mixtures of chemical reaction solution, we suppose that the temperature coefficient of its effective permittivity is the complicated function of the reciprocal of temperature.

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

where, the complicated function f(1/T) should be continuous function; T is temperature; ε_{eff} is effective permittivity. When we expand f(1/T) into the Maclaurin series, f(1/T) can be written as follows:

$$f\left(\frac{1}{T}\right) = f(0) + \frac{f'(0)}{1!} \cdot \frac{1}{T} + \frac{f''(0)}{2!} \cdot \frac{1}{T^2} + \cdots + \frac{f^{(n)}(0)}{n!} \cdot \frac{1}{T^n} + \cdots \tag{2}$$

Because the chemical reactants change with not only temperatures but also the reaction time during the microwave heating, the reactant to be virtual mixture and its effective permittivity is decided only by its composition and temperature. So,

$\frac{f^{(n)}(0)}{n!}$ should be related to the reaction concentration and f(1/T) is related to reaction concentration and temperature. At last, the f(1/T) should be the following form:

$$f\left(\frac{1}{T}\right) = \alpha_1(C) + \alpha_2(C)\cdot\frac{1}{T} + \alpha_3(C)\cdot\frac{1}{T^2} + \cdots + \alpha_n(C)\cdot\frac{1}{T^n} + \cdots \quad (3)$$

here, C is the concentration of reactant and $\alpha_n(C)$ means the functions decided by experiment data. Finally, we used this formula to calculate the effective permittivity of mixtures during the microwave heating on the chemical reaction by means of the measured effective permittivity at the constant temperature.

EXPERIMENTAL

In present experiment, we use a microwave vector network analyzer of Agilent E8362B to measure the reflection coefficients from a special designed coaxial line probe[6]. The gold-plated probe was inserted in the reactant in the experiment. The measurement was performed at 2450 MHz. The height and diameter of the beaker must be larger than three wavelengths at the measurement frequency to get accurate results. A dielectric stirrer was used to make the solution homogeneous. The temperature of the solution in beaker was carefully controlled by using of KXS-A trough and measured by UMI-8 optical fiber thermometer. The figure of experiment system is shown in Fig. 1.

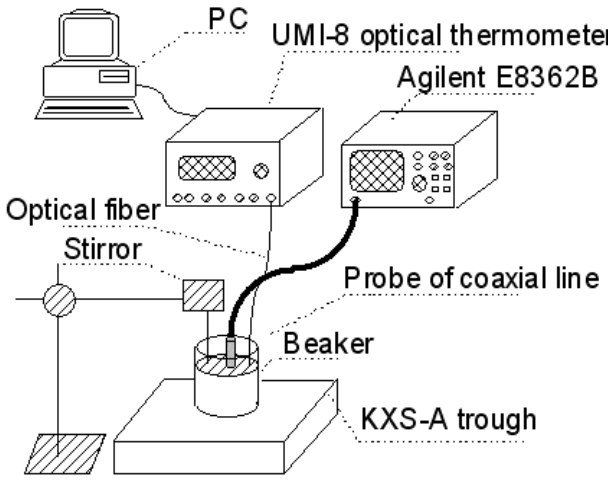


Fig. 1. Experimental system

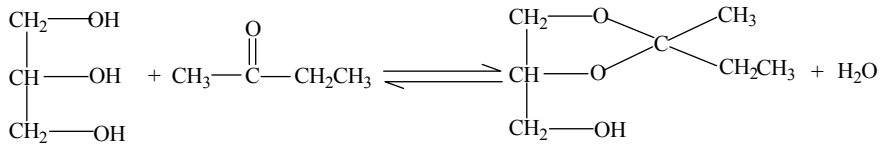
Acetone iodination reaction and condensation of glycerol with butanone were widely used to study the chemical kinetics[7,8]. To corroborate this method, the chemical reactions were employed.

The acetone iodations reaction equation is written as follows:

$$KIO_3 + 5KI + 6HCl + 3CH_3COCH_3 \xrightarrow{k} 3CH_3COCH_2I + 6KCl + 3HI + 3H_2O \quad (4)$$

The initial concentrations are C_{KIO_3} = 0.08 mol L^{-1}, C_{KI} = 0.04 mol L^{-1}, C_{HCl} = 1.0 mol L^{-1} and $C_{CH_3COCH_3}$ = 4.0 mol L^{-1}. The reaction was carried out at four constant temperatures of 30, 37, 44 and 52 ºC, respectively.

The condensation of glycerol with butanone reaction equation is written as follows:



(5)

The initial concentrations are $C_{C_3H_8O_3}$ = 6.77 mol L^{-1}, $C_{C_3H_8O}$ = 5.78 mol L^{-1}, $C_{C_5H_6}$ = 0.99 mol L^{-1} and 10.45 g of *p*-toluenesulfonate as catalyst. The reaction was carried out at four constant temperatures of 25, 35, 40 and 45 ºC, respectively.

RESULTS AND DISCUSSION

In the first experiment, the reflection coefficients were sampled per 15 s automatically. We developed a GA-based inverse calculation technique and employed it to determine the complex permittivity of the solution from the measured reflection coefficients[6]. Since the initial concentrations of reactants, their proportion and the dynamic equation of the reaction are known, we can calculate the concentrations of each reactant and resultant at any sample point. Besides, all the concentrations can be expressed by the concentration of a reactant or resultant. Therefore, C_{KI} as the base concentration is choosen to express other concentrations according to the reaction kinetics equation. When the proportion of reactants are given, the effective permittivity can be determined by temperature T and C_{KI}. Then a fitting formula was obtained in terms of the experimental data by the following steps.

In order to reduce initial experimental errors, the measurement started from the third sampling time for the reaction under 30 ºC and from the second sampling time at 37, 44 and 52 ºC, ending at the reaction equilibrium time. Randomly select three measuring curves at three temperatures for fitting formula, leaving the fourth measuring curve to verify the obtained formula. Here we select measuring curves at 30, 37 and 52 ºC for formula fitting and measuring curve at 44 ºC for checking. In the fitting formula of this reaction, positive-power exponential form, power function, trigonometric function and hyperbolic function can be employed here. When compared with a quite number of fitting formulas, the optimal form is determined as:

$$\varepsilon_{eff}' = a \cdot C^b \cdot T + g/T \quad (6)$$

where, ε_{eff}' means the real part of effective permittivity, a = -0.26322, b = -13.69014 and g = 47547.04977.

Similarly, the fitting formula for the imaginary part of permittivity of acetone iodination reaction can be expressed as

$$\varepsilon_{eff}'' = \exp(a \cdot C) / T + b \cdot C^{g}/T \quad (7)$$

where, ε_{eff}'' means the imaginary part of effective permittivity, a = 26.29100, b = 2011.49400 and g = -0.21430.

It can be seen in Fig. 2a and 2b that the fitted lines agree well with the measured data.

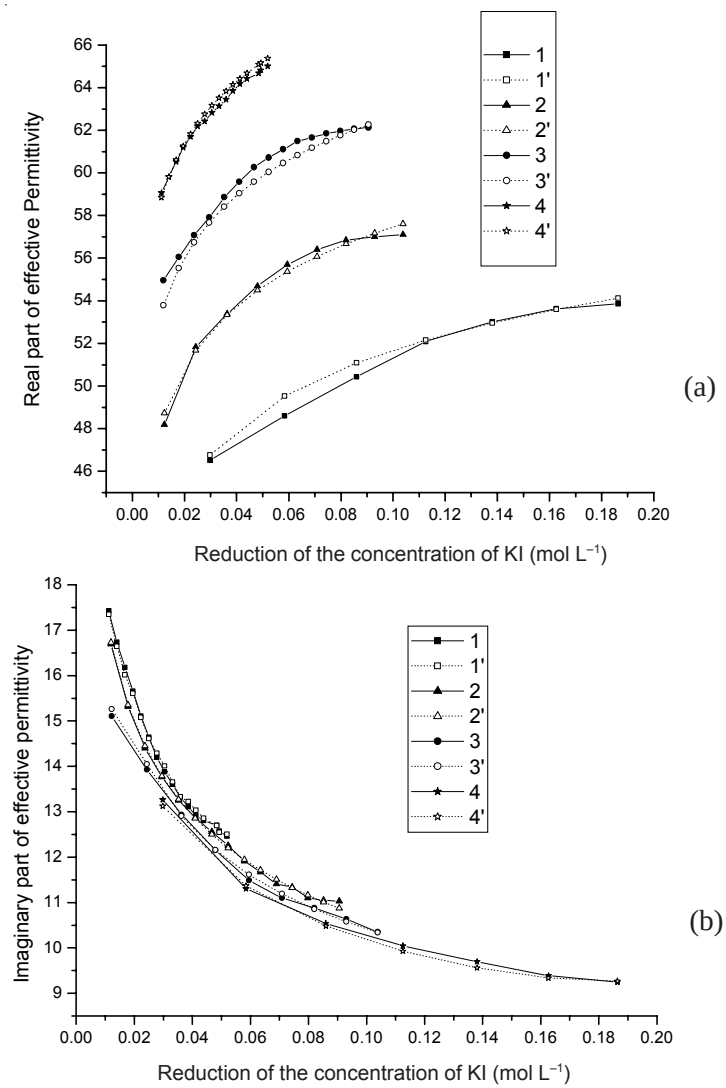


Fig. 2. (a) Real part of permittivity of acetone iodations reaction, (b) Imaginary part of permittivity of acetone iodination reaction
Note: 1 = 30 ºC measured; 1' = 30 ºC fitted; 2 = 37 ºC measured; 2' = 37 ºC fitted; 3 = 44 ºC measured; 3' = 44 ºC fitted; 4 = 52 ºC measured; 4' = 52 ºC fitted

Further, condensation of glycerol with butanone is used to validate the foresaid method. With the same steps (measuring curves at 25, 35 and 40 ºC for formula fitting and measuring curve at 44 ºC for checking), we obtain the fitting formula as follows:

$$\varepsilon_{eff}' = a \cdot C^{b} \cdot T + d^{c} \cdot g/T \quad (8)$$

where C is concentration of $C_{C_3H_8O}$, a = -0.03580, b = -0.00919, d = 6618.44993, g = 1.00283.

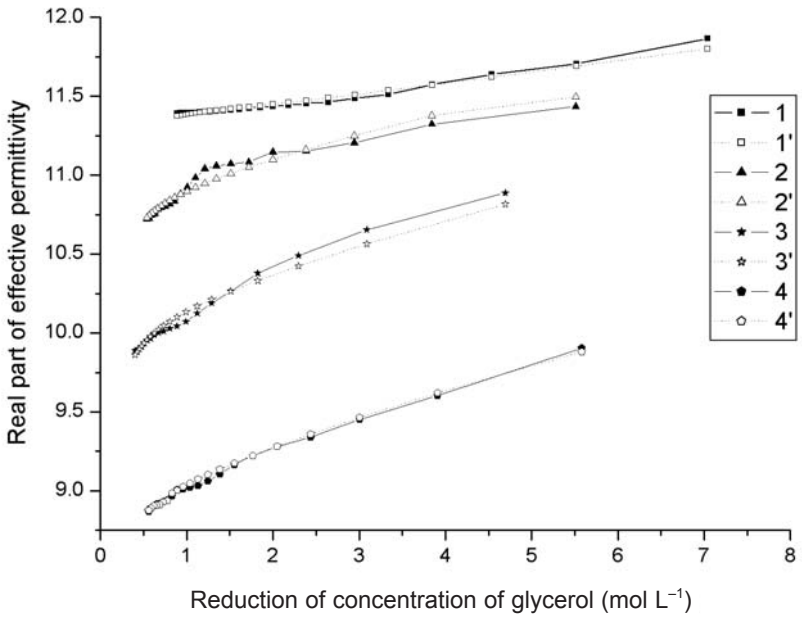
$$\varepsilon_{eff}'' = \frac{a}{C^{b}} / T + d^{\exp(C)} \cdot g \cdot T^{2} \quad (9)$$

where a = -1268.47168, b = -0.0631, d = 1.00000, g = 0.00020.

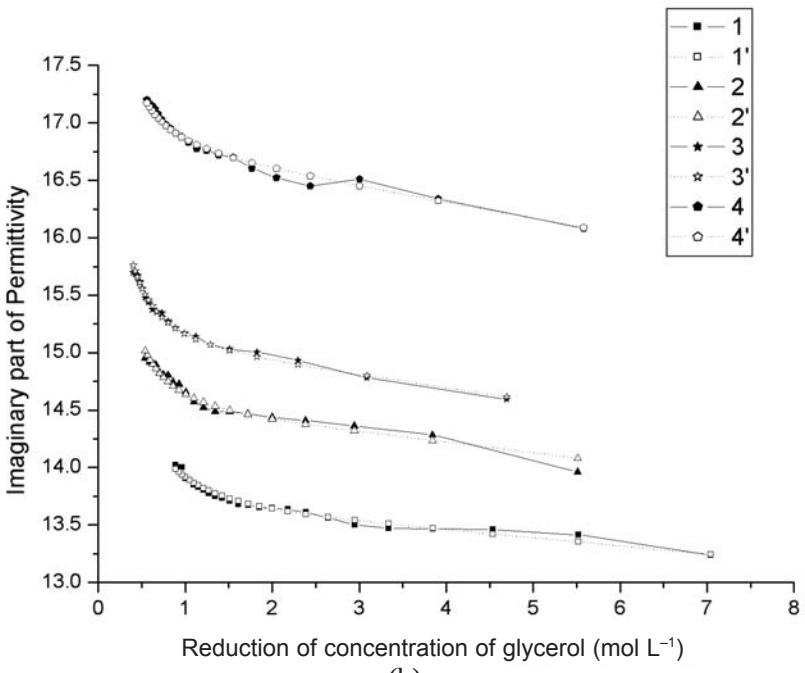
In the fitting formula above, $1/C^{b}$ is reasonable because the reaction above is an organic reversible reaction.

As for the fitting formula for real part of condensation of glycerol with butanone reaction, error of fitting in most of the measuring points is less than 0.4 %, with the maximum error of 1.34 %; while as for the imaginary part, error of fitting in most of the measuring points is less than 0.3 %, with the maximum 0.968 %. Therefore, the fitting results is quite sound (Fig. 3a and 3b).

When these fitting formulas are obtained, a series of 3-dimension graphs can be drawn, such as 3-dimension graphs for real part and imaginary part of condensation of glycerol with butanone reaction (Figs. 4 and 5). It shows that the 3-dimensional graphs indicate effective permittivity during the microwave heating on chemical reactions under the any temperature and concentration with the precondition that all the reactants are in the same proportion as the 3-demensional graphs suggest.



(a)



(b)

Fig. 3. (a) Real part of permittivity in condensation of glycerol with butanone reaction
(b) Imaginary part of permittivity in condensation of glycerol with butanone reaction
Note: 1 = 25 ºC measured;1' = 25 ºC fitted;2 = 30 ºC measured; 2' = 30 ºC fitted; 3 = 40 ºC measured; 3' = 40 ºC fitted; 4 = 45 ºC measured; 4' = 45 ºC fitted

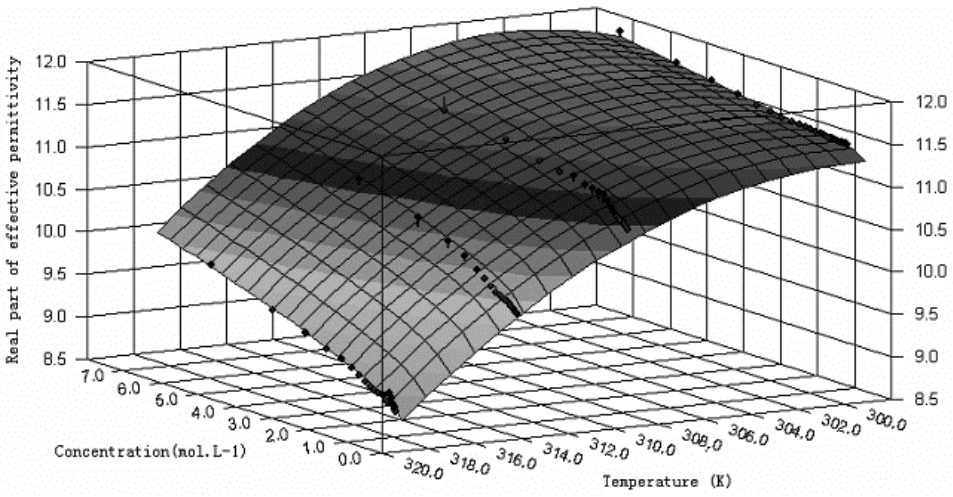


Fig. 4. Three-dimension graph of real part of permittivity in condensation of glycerol with butanone reaction

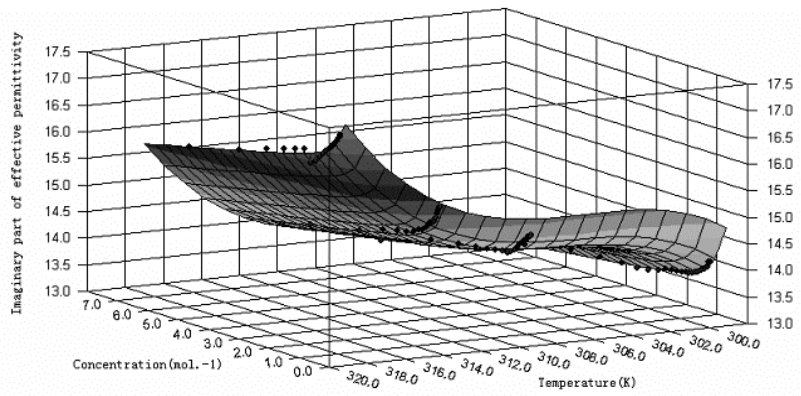


Fig. 5. Three-Dimension graph of imaginary part of permittivity in condensation of glycerol with butanone reaction

It is observed, as expected, that the change of effective permittivity is faster at higher temperature than the one at lower temperature. The values of the real and imaginary part of effective permittivity at lower temperature are larger than the values at higher temperature.

Conclusion

Based on experimental results, the effective permittivity during microwave heating on chemical reactions at any temperature and concentration can be calculated by the simple method. To corroborate this method, two chemical reactions were employed. The calculated results of effective permittivity of the mixtures are in good agreement with the measured results. The calculation of effective permittivity makes it possible to analyze the interaction between microwave and the chemical reactions.

ACKNOWLEDGEMENTS

This project was supported by National Science Foundation of China under Grant No. 60531010 and Research Fund for the Doctoral Program of Higher Education of China under Grant No. 20070610120.

REFERENCES

1. Q.H. Jin, S.S. Dai and K.M. Huang, Microwave Chemistry, Sciences Press, Beijing (1999).
2. M. Chen, J.W. Hellgeth, E.J. Siochi, T.C. Ward and J.E. Mcgrath, *Polym. Eng. Sci.*, **33**, 1122 (1993).
3. J. Baker-Jarvis and R. Inguva, *J. Microwave Power Electromag. Energy*, **23**, 160 (1984).
4. H. Zhang and A.K. Datta, *J. Microwave Power Electromag. Energy*, **35**, 71 (2000).
5. A. Sihvola, Electromagnetic Mixing Formulas and Applications, The Institution of Electrical Engineers, London (1999).
6. K.M. Huang, X.J. Cao, C.J. Liu and X.B. Xu, *IEEE Trans. Microwave Theory Techniq.*, **51**, 2106 (2003).
7. F. Daniels, R.A. Alberty, J.W. Williams, C.D. Cornwell, P. Bender and J.E. Harriman, Experimental Physical Chemistry, Mcgraw-Hill, Inc., New York (1975).
8. O. Levenspiel, Chemical Reaction Engineering. Wiley, New York (1999).

(*Received*: 30 December 2008; *Accepted*: 30 April 2009) AJC-7525