

Permittivity Measurements of Mixtures as a Function of their Composition for Microwave Heating Improving

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Microwave heating is a more efficient alternative to conventional heating in the chemical reactions field due to its positive effects on conversion and reaction kinetics. Dielectric properties of substances and mixtures are important for the optimization of microwave heating processes; notwithstanding this, specific databases are poor and far from being complete, and in the scientific literature only a few data regarding these properties can be found. Dielectric properties are represented by permittivity, which is a complex measure of a substance behaviour in the presence of an electromagnetic field and depends on the field frequency, as well as on the temperature and composition of the chemical system under study. In this work, some real and imaginary parts of permittivity measurements were carried out using a specially designed measurement system. The apparatus was tested in the estimation of permittivity values in water-ethanol mixtures, varying their composition. The results were compared to literature data and fitted with available literature models to verify their trend as a function of composition. The permittivity real part values increase with reducing the molar fraction of ethanol, whereas the imaginary part decreases, according to the values of water and ethanol permittivity reported in the literature. The regressions carried out to describe the permittivity dependence on composition prove that the measured values can be well described by the models taken into account.

1. Introduction

Microwave (MW) heating is a characteristic phenomenon that cannot be imitated by other heating methods: it can lead to internal heating, selective heating, the formation of hotspots, local heating, superheating, and non-uniform heating (Horikoshi et al., 2018). Microwaves are able to generate heating by a loss of energy which is then absorbed in the form of thermal energy. MW irradiation is the simplest, most inexpensive and efficient unconventional heating method available in the applied chemistry field.

Effective use of microwaves can lead to an increase in the heating efficiency of processes (Horikoshi et al., 2018). The advantages of microwave heating, compared to conventional ones, are an important reduction of reaction times, milder reaction conditions and an increase of product yields and purities (de la Hoz et al., 2005). In addition, using of this kind of heating makes the process more controllable and safer, also reducing the complexity of the exchange units. This non-classical heating technique has slowly moved from a laboratory scale approach to an established method that is now heavily used also in industrial applications. The advantages of microwave heating associated with reaction chemistry have been exploited in several fields, including organic and pharmaceutical chemistry, solid-phase peptide and polymer synthesis, material science, nanomaterials research (Kappe, 2013) and a variety of chemical (Fanti et al., 2016) and biochemical processes, like enzyme reactions (Casu et al., 2015) and disinfection (Desogus et al., 2016). Dielectric properties influence the reflection of electromagnetic waves at interfaces and the attenuation of the wave energy within materials, so determining the amount of energy which can be absorbed and converted into heat. Dielectric properties of materials related to the interactions with microwaves are permeability, permittivity and electrical conductivity. It is generally accepted that, for most dielectric materials, the permeability presents no or very small contribution to dielectric heating, and so it is usually not considered (Zhang and Datta, 2001). Knowing the value of permittivity, on the

contrary, is useful to estimate the reaction temperature (Kappe, 2013), and to optimize the heating process in order to minimize energy consumption. Also, the penetration depth of the material is an important parameter for the heating processes efficiency improvement, and it depends on the dielectric properties of the substance (Marra et al., 2009). According to what above reported, in addition to chemistry, the knowledge of material dielectric properties is useful to improve MW heating in other interesting fields like, for example, food technology (Datta, 2001), pyrolysis (Desogus et al., 2016c), hyperthermia cancer treatments (Fanari et al., 2018) and sterilization of agricultural lands (Fanti et al., 2017).

Notwithstanding their potentially great importance, there is a big lack of fundamental data on the dielectric properties of substances and materials, which generates several difficulties with the scaling up from laboratory units to industrial equipment. The goal of this work is to provide some useful information about the dielectric properties of a water-ethanol system, which can be representative of many typical solvents of industrial interest, due to the common use of the alcohols in the organic chemistry. The measurement method and the collected information suggest how the dielectric characterization of pure substances and binary mixtures can be done with the purpose of the reaction process optimization and the minimization of its energy consumption.

2. Permittivity

Permittivity is a very important parameter, useful to characterize the behaviour of a material when exposed to an electromagnetic field. More in detail, permittivity represents the ability to store electrical energy of a non-conductive material subjected to an electrical field (Lvovich, 2012). In the frequency domain, this parameter (ε) is expressed as:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (1)$$

where ε' and ε'' are the real part and the imaginary one, and j is the imaginary unit. The real part of permittivity (ε') is also known as the dielectric constant and it represents the energy stored from a material while exposed an electrical field. The imaginary part of permittivity (ε''), instead, is related to the energy loss and so it is known as loss factor. The real part of permittivity is linked with the so called "polarization phenomena": the greater ε' value corresponds to the greater capacity to store electromagnetic energy due to the electronic charge orientation with respect to the field (Nollet, 2017). Polarization phenomena in materials can be of electronic, atomic and orientation type (Kremer and Schonhals, 2012). The first two kinds are induced by the applied field and caused, respectively, by the electron mobility inside the atom, and of the atoms inside the molecule. The third one exists only in polar materials. Typically, the electronic polarization persists up to frequencies of the order of 10^{16} Hz, the atomic polarization up to about 10^{13} Hz, while the dispersion for the orientation polarization can occur in a wide frequency range, approximately 10^2 - 10^{10} Hz, which depends on the material conductivity and temperature (Kremer and Schonhals, 2012). A perfect insulator has a great value of ε' and its electric charge can instantly react to the field by orientating in according to this. However, most of the materials present a phase delay between the dipole alignment and the appearance of the electromagnetic field, so part of the radiation energy is converted into thermal one. At radio and microwave frequencies, ionic conduction and dipole rotation are the dominant loss mechanisms (Ryynänen, 1995). Dielectric losses are linked to ε'' , so if a material with a high value of ε'' is considered, this will absorb less energy, so it would require more energy to be heated with respect to a material with a lower value of ε'' (Marra et al., 2009). For example, water and polar substances have high values of the real part of permittivity, whilst electrolytes are characterized by higher values of the imaginary part.

The parameters that mainly affect permittivity are frequency and temperature. Moreover, permittivity depends also on the material composition (Desogus et al., 2016) and texture (Casu et al., 2018), and to a lesser extent, on pressure (Von Hippel, 1954). The frequency influence, in the case of pure liquids, is described by the Debye model (Debye, 1929):

$$\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_S - \varepsilon_{\infty}}{1 + \omega^2\tau^2} - j \frac{(\varepsilon_S - \varepsilon_{\infty})\omega\tau}{1 + \omega^2\tau^2} \quad (2)$$

where ε_{∞} is the constant value of permittivity reached at optical frequencies (infinite frequency), ε_S is the static permittivity, i.e. the constant value of permittivity at zero frequency, ω is the radiation frequency, and τ is the relaxation time of the material. The relaxation time is a measure of the polarization ability of the material, as it represents the time delay on the material response to an electric field change; this parameter is correlated to the molecular conformation and, in general, increases with the dimension of molecules (Komarov et al., 2015). The temperature dependence of permittivity is due to the increasing in the mobility and agitation of molecules induced by heating that leads to changes in the polarization ability and in the relaxation frequency value. Polarization is inversely proportional to the absolute temperature, as it induces reorienting, and so it plays an opposite role with respect to the thermal disordered motion phenomena. According to this, the material

temperature increases under an electromagnetic field is proportional to the dielectric loss factor, to the squared field intensity, to the exposure time and to the radiation frequency, and it can be calculated by the following expression (Komarov et al., 2015):

$$P_v = 2\pi f \cdot \varepsilon_0 \cdot \varepsilon'' \cdot E^2 \quad (3)$$

where P_v is the produced volume specific thermal power, f is the frequency, ε_0 is the free space permittivity, and E is the electric field intensity.

3. Permittivity measurements

3.1 Fundamentals of the measurement technique

Several techniques for permittivity measurement are available, but all methods have limitations in terms of sample kind and especially in the frequency range. However, in order to extract some information on relaxation processes, it is paramount to measure the dielectric permittivity in a wide frequency range.

Alcohols or other dielectric liquids can be considered as good solvents for a number of biological molecules, body tissues, blood and bone marrow. Therefore, an in-depth permittivity study of various common solvents is essential for chemical and biomedical researches. A number of techniques have been developed to be used for the measurement of the complex permittivity of liquids. For instance, the most commonly used techniques are coaxial line measurements and capacitive techniques; also the waveguide, the open-ended waveguide, the open-ended coaxial line, the dispersive Fourier transform spectroscopy (DFTS), and the microwave resonant methods have been applied (Wang and Afsar, 2003). In the case of the present study, the parallel plate technique was used. The main advantages of this technique are that it is easy to use, non-destructive, fast and characterized by a reasonable accuracy ($\pm 5\%$) (Barba and d'Amore, 2012). To perform the measurement by this technique, the sample is packed between two electrodes, as a means of realising an electric condenser, so the value of permittivity is estimated from impedance measurements obtained with the use of an impedance analyzer or an LCR meter (Nollet, 2017). Specifically, in this work, an impedance analyzer was used. This kind of instrument measures the transmission and reflection characteristics of devices and networks through the application of a known swept signal (sinusoidal signal with time-variable frequency) and the measurement of the system response. After this, the analyzer compares the signal transmitted or reflected from the device under test with the transmitted signal and converts the reflection measures into impedance measures. In particular, the impedance values were calculated using the following equation (Bao et al., 1994):

$$Z_R = Z_0 \frac{1 + S_{11}}{1 - S_{11}} \quad (4)$$

in which Z_R is the impedance of the measuring cell, Z_0 is the reference impedance of the instrument calculated by means of its calibration process, and S_{11} is the reflection coefficient that takes into account the electromagnetic waves which are reflected by the measurement device. To correlate the impedance measures with the dielectric ones, the following expression derived from the dielectric theory (Lvovich, 2012) were used:

$$\frac{\varepsilon'}{\varepsilon_0} \propto C \quad (5)$$

$$C = \frac{1}{\omega X} \quad (6)$$

$$\frac{\varepsilon''}{\varepsilon_0} \propto \frac{1}{R} \quad (7)$$

$$Z = R + jX \quad (8)$$

where C is the capacitance, R is the resistance and X is the reactance of the system. In fact, the dielectric constant is inversely proportional to the reactance while the loss factor is inversely proportional to the resistance. So, it was chosen to build two calibration straight lines, one where ε' is a function of the inverse of reactance, and one where ε'' is a function of the inverse of resistance, taking as the references two substances with known values of permittivity. Thus, after building the straight line passing through the known points, the value of permittivity of the different mixtures was estimated.

3.2 Design of the parallel plate cell

The parallel plate system (shown in Figure 1), connected to the impedance analyzer, is a cell, the body of which is made of plastic material (PVC). The cell consists of two circular electrodes of 30 mm diameter made of copper and spaced of 6 mm. In the volume included between the two copper plates, the liquid sample is inserted.

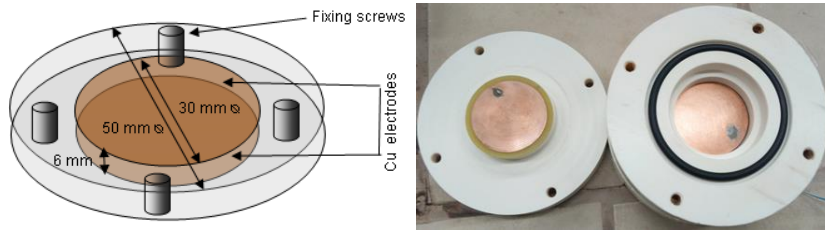


Figure 1: Sketch and picture of the measuring cell.

3.3 Experimental

The impedance analyzer used in this work was a Vector Network Analyser (Hewlett-Packard, model 8720C). This instrument works in the range of frequencies between 50 MHz e 20 GHz, with a frequency resolution of 100 KHz. The cell was linked with the analyzer through a coaxial cable and an SMA connector. Because of their different structures and varying dynamic responses to the external field, each material shows a unique complex dielectric spectrum in the radio- microwave frequency range. Analyzing the frequency spectra of R reported in Figure 2, and of X in Figure 3, it is easily observable that the maximum differences of these values among the various mixtures are located in the maximum peak zone for R and in the minimum peak zone for X .

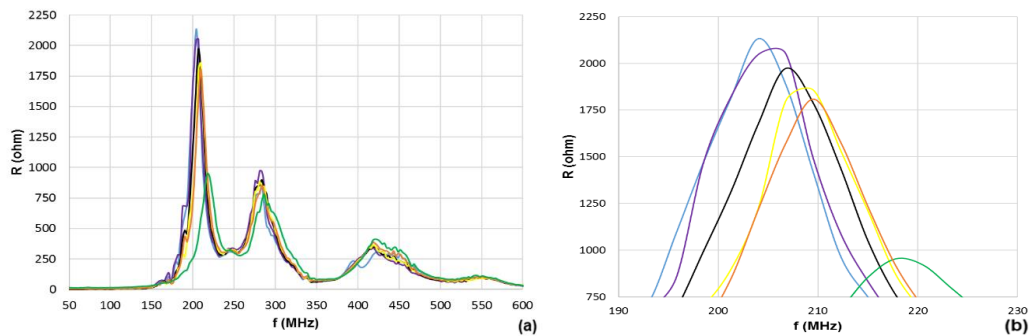


Figure 2: Spectra of R values (a) and values of the maximum peaks in the restricted range considered for the measurements (b), for water (—), 1-propanol (—) and the water-ethanol mixtures with ethanol molar fraction of $X_{Eth}=0.007$ (—), $X_{Eth}=0.219$ (—), $X_{Eth}=0.495$ (—), $X_{Eth}=0.854$ (—).

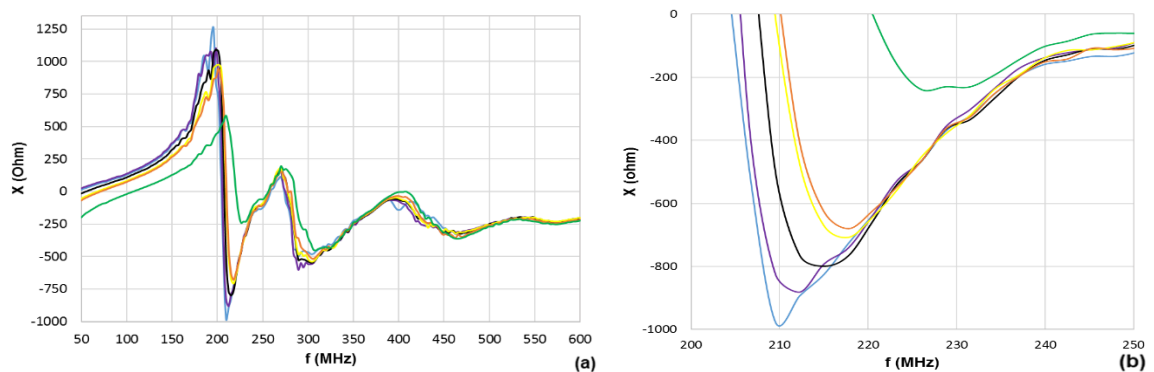


Figure 3: Spectra of X values (a) and opposite values of the minimum peaks in the restricted range considered for the measurements (b), for water (—), 1-propanol (—) and the water-ethanol mixtures with ethanol molar fraction of $X_{Eth}=0.007$ (—), $X_{Eth}=0.219$ (—), $X_{Eth}=0.495$ (—), $X_{Eth}=0.854$ (—).

According to this, a first indication can be obtained focusing the attention to these peak values of R and X , and in this work, only the maximum values (for R) and the minimum values (for X) have been considered. Water-ethanol mixtures with different composition were prepared and measured. Before carrying out the measurements, the calibration straight lines were built using water and 1-propanol with known permittivity values as references, so the measuring range was between 77.5 and 16 for ε' and between 6.325 and 1.24 for ε'' (values of the permittivity of the pure substances) (Von Hippel, 1954).

4. Results and conclusions

The values of the permittivity of the water-ethanol mixtures are reported in Figure 4, where it is possible to observe the trend of $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ as a function of composition. As we can see from the graphs, the trend as a function of composition is near to be linear both for ε' and ε'' . We also compared some values of ε' for different compositions to the water-ethanol mixtures data reported in the literature (Dortmund Databank, 2015). The estimated values are more different near the median compositions and less in the ranges with high water concentration or high ethanol concentration. However, the overall differences are quite small and the trend is very similar, so it is possible to deduce that the measurement technique is reliable and sufficiently accurate. Regarding the values of ε'' , it was not possible to make a similar comparison due to the lack in the literature about the values of this parameter for the same binary system.

Moreover, the experimental data were fitted by using a literature model by Acree (1992), in the form given by Jouyban et. al. (2004), which seemed to be the most appropriate for the case under study (binary mixture with water and alcohol). The model equation is the following:

$$\ln \varepsilon' = X_{Eth} \ln \varepsilon'_{Eth} + (1 - X_{Eth}) \ln \varepsilon'_W + X_{Eth}(1 - X_{Eth}) \sum_{i=0}^2 K_i (X_{Eth} - (1 - X_{Eth}))^i \quad (9)$$

where X represents the molar fraction, the subscripts "Eth" and "W" stand for ethanol and water, and K_i are the model parameters. For the specific case under study, the permittivity real part values for the pure substances are $\varepsilon'_W/\varepsilon_0 = 77.5$ and $\varepsilon'_{Eth}/\varepsilon_0 = 22.3$. Even if in the cited literature the model was applied only to the real part of the permittivity, in the present work it was used, with good results, also for the imaginary one, just substituting ε'' to ε' in Eq(9) and considering that, for the pure substances, the permittivity imaginary part values are $\varepsilon''_W/\varepsilon_0 = 1.24$ and $\varepsilon''_{Eth}/\varepsilon_0 = 5.62$.

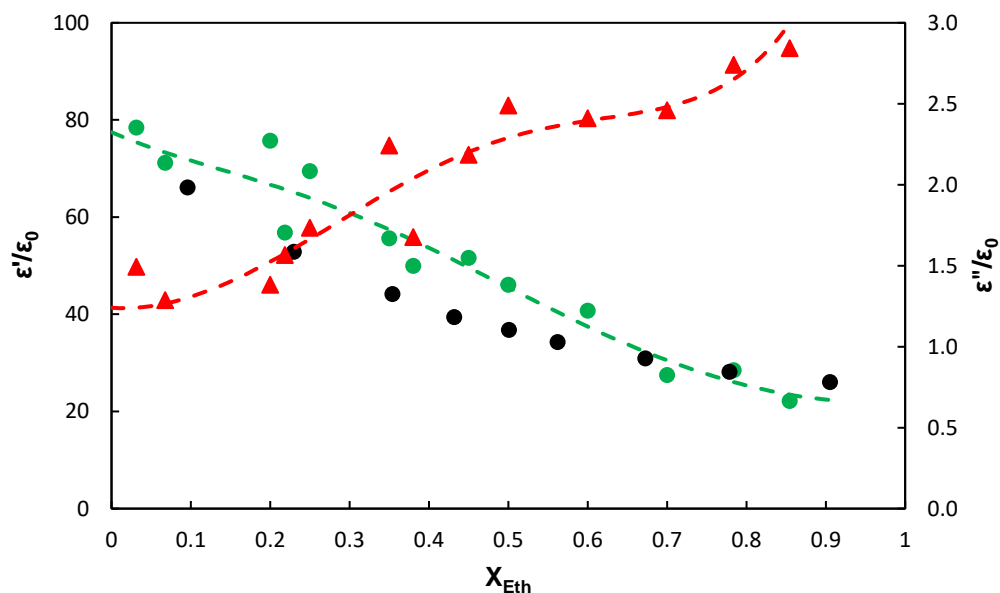


Figure 4: Measured (\bullet) and literature (Dortmund Databank, 2015) (\bullet) $\varepsilon'/\varepsilon_0$ values and measured values of $\varepsilon''/\varepsilon_0$ (\blacktriangle) for the water-ethanol mixtures, reported as a function of the ethanol molar fraction (X_{Eth}); Acree model curve for $\varepsilon'/\varepsilon_0$ (-) and $\varepsilon''/\varepsilon_0$ (-) as a function of the ethanol molar fraction (X_{Eth}).

As a future goal of the work, it would be interesting to extend this approach to other mixtures and to develop proper modelling in order to describe possible similitudes and/or differences between similar or different

substances. In fact, a deeper knowledge about the dielectric behaviour of complex systems would be very helpful to make heating and reaction processes more and more selective and efficient, so contributing to the minimization of their energy consumption and environmental impact.

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