

# TEMPERATURE DEPENDENCE OF DIELECTRIC RELAXATION OF SOLVENT MIXTURES

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## INTRODUCTION

Microwave heated process design and implementation requires quantitative data on chemicals dielectric properties or at least methods for their prediction. There have been several investigations on the dielectric behaviors of solvent mixtures [1-3] in which dielectric relaxation spectra were used to examine molecular orientations, hydrogen bonded networks and microdynamics of these systems.

In this paper, we report the temperature dependent dielectric properties of ortho-nitrotoluene and para-xylene mixtures at microwave frequency (2450 MHz). These evolutions have been measured in the temperature range  $20^{\circ}\text{C} \leq T \leq 100^{\circ}\text{C}$  and in the mole fraction range  $0 \leq x \leq 1$ , with T the temperature and x the mole fraction of o-nitrotoluene in p-xylene. In a recent paper [4] we present a brief survey of our measuring equipment. Dielectric parameters were carried out by the method of small perturbations in a resonant cavity. Based on Debye theory, the dielectric measurements allow to determine the relaxation times of these different mixtures.

## THEORY

Debye [5] showed that if one modeled a polar liquid to consist of a spherical dipoles oscillating in a continuous viscous medium, then the dependence of the complex permittivity  $\varepsilon$  on the angular frequency  $\omega = 2\pi f$  (the units of  $\omega$  are rad.Hz and respectively Hz for the frequency f) of the imposed electro-magnetic field is given by:

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

where  $\varepsilon_s$  is the static permittivity,  $\varepsilon_{\infty}$  is the so-called infinite frequency permittivity that is to say, the limit of  $\varepsilon$  as the frequency of the imposed electro-magnetic field tends to infinity and  $\tau$  (expressed in s) is the Debye relaxation time.

The fundamental quantities  $\varepsilon_s$  and  $\varepsilon_{\infty}$ , depend only on the molecular state of the medium not on the electro-magnetic field, so they ought to be calculable in terms of molecular

concepts.

The relaxation time,  $\tau$ , has the following significance. The application of a static electric field to a solution containing polar molecules will have the effect of aligning the molecules in the direction of the external field. If the field is switched off the molecules do not immediately adopt random orientations. The relaxation time is a measure of the time taken to achieve this randomized state. The relaxation time depends critically on the nature of the functional groups and the volume of the molecule. Functional groups capable of hydrogen bonding have a particularly strong influence on the relaxation times. The relaxation times of solvents decrease as the temperature of the solvent is increased.

## **REACTANTS**

The reactants, ortho-nitrotoluene and para-xylene, have been studied separately. The thermal behavior of the dielectric constants shows that they are rather constant in the temperature range and can be approximated to 2.1 and 9.8 respectively to p-xylene and o-nitrotoluene.

P-xylene is a symmetrical molecule which means that its dipolar moment equals zero. Dielectric loss of this component confirms p-xylene is apolar. For o-nitrotoluene, polar molecule, dielectric loss decreases from 2.5 to 1 between 20 °C and 100 °C.

## **RESULTS AND DISCUSSION**

We determine the dielectric properties of o-nitrotoluene and p-xylene mixtures from 20 °C to 100 °C and for different mole fractions.

From the evolution of dielectric loss as a function of dielectric constant. It may be noted that dielectric constant whatever the molar fraction doesn't depend on the temperature. Nevertheless, dielectric loss decreases with rise in temperature. At constant temperature, both dielectric constant and loss with rise in o-nitrotoluene molar fraction, increase.

On the other hand, dielectric loss linearly increases with dielectric constant at constant temperature and with rise in molar fraction.

Based on Debye theory, these results permit to deduce that the relaxation time  $\tau$  doesn't depend on the mixture composition but depends only on the temperature. Finally the evolution of the relaxation time of the investigated system is found to decrease with rise in temperature (from 20 ps to 8 ps between 20 °C and 100 °C) and this is in conformity with the Debye equation of polar molecule. The rise in temperature affects dipolar moments polarization: dipoles orientation would be more difficult because of the thermal agitation. When the polarization is modified, the relaxation time is modified too.

## **CONCLUSION**

In the case of a frequency controlled magnetron, the knowledge of relaxation time behavior with temperature permits the prediction of energy conversion inside the

medium.

Further researches are required to optimize microwave heating, in a recent study [6] we illustrate the importance of resonant modes for optimal energy conversion. The relaxation time plays again an important role for the determination of essential parameters as penetration depth, wavelength inside the medium and finally modes localization.

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