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Microwave dielectric properties of binary solvent water-alcohol, alcohol-alcohol mixtures at temperatures between -35°C and +35°C and dielectric relaxation studies

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Abstract: In this work, our objective was to study the complex permittivity of binary mixtures of water-ethanol, water-methanol and methanol-ethanol with various mole fractions at temperature between -35 and 35 °C. Measurements were made in the frequency domain from 300 kHz to 1.3 GHz by means of an open ended coaxial line technique coupled to a network analyzer. Water-ethanol and water-methanol mixtures display a Kraszewski Law while methanol-ethanol mixture shows a Shivola-Kong Law. The static dielectric constant, ε_s were obtained from the plateau of $\varepsilon'(\omega)$ curve, in water rich mixture or alcohol rich mixture has similar real permittivity ε' of pure liquids. The values of ε_s mixtures increase by decreasing the temperature assigned to the cooperative dynamics H-bond system in mediums. The validity of permittivity measurements according to the temperature are verified by the Queen-King Law and the $A_{j(0\leq j\leq 2)}$ constants are compared with literature data. The dielectric relaxation behaviour of water-ethanol mixture can be better described with a Cole-Davidson function while for methanol-ethanol one, a Debye function gives a good fit. At 25 °C, the relaxation time τ in the aqueous mixtures of ethanol and methanol sharply increased with increasing alcohol concentration.

Keywords: mixture solvent**,** open ended coaxial line, dielectric properties, permittivity, relaxation time.

Introduction

The study of the permittivity complexes liquid compounds or solids leads to relatively important data relating to a variety of scientific fields i.e. chemistry, physics, biology, electronic engineering and civil engineering [1].

According to Aghaie et al.[2] the major physical-chemical properties of solutions are influenced by the solvent's dielectric constant. The permittivity represents a fundamental parameter in the determination of the properties dielectric, thermodynamic, electrochemical, structural which governs a given solution [3]. Many investigations toward a better understanding of the unusual characteristics of water as liquid and solvent have been performed using selected alcohols as probes[4]. For example,

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the dielectric properties of water-alcohols and alcohol-alcohol binary mixtures have received much interest by Bertolini et al.[5] They noted that the variation of the dielectric properties, with the composition and the temperatures, provides important information on the intermolecular interactions and on the molecular structure of the mixture solvent. Moreover, the mixtures water-alcohol and alcohol-alcohol belong to a new generation of miscible solvents of an interest major in pharmaceutical industry. Indeed, these mixtures make it possible to understand the mechanism and the stability of the solubility of drugs.

According to Bao et al.[6], both Debye and Cole-Davidson functions could be used to determine the dispersion parameters for water – methanol mixtures.

Cole-Cole, Cole –Davidson and Havriliak-Negami functions were used by Sato and Buchner [7] to fit the spectra of water- alcohol mixtures. However, for methanol –ethanol mixtures, gives a good fit to the entire real part and most of the imaginary part.

Recently Y. S. Joshi et al. [8], have studied the dielectric relaxation for water-alcohol mixtures using time domain reflectometry. They concluded that the double relaxation times, primary process ($\tau 1$) and secondary process ($\tau 2$) have been observed.

The distribution of the relaxation time of alcohol-water mixtures was also studied by Sudo et al.[9]. The authors observed asymmetric dielectric losses for water and 22 aliphatic alcohols at different concentrations. Each mixture shows the minimum value of the parameter for the asymmetrical broadness and the maximum relaxation time value at certain concentration.

The aims of this work were to understand the influence of the temperature and the composition of mixture on the variation of the complex permittivity and the dielectric relaxation processes. Indeed, these last are relatively sensitive to the molecular structure of the mixture solvent to study and can be used to obtain information on the process of molecular reorientation they are also related to the concentration of the constituent species (laws of mixture).

In this work, we will also present a comprehensive dielectric characterisation of binary mixtures water-ethanol, water-methanol and methanol-ethanol for various mole fractions in the whole concentration range. Complex dielectric constants were measured at temperature between -35 and 35 °C in the frequency range from 300 kHz to 1.3 GHz with a network analyzer (HP8712ES) using the open-ended coaxial probe technique, which is very convenient for liquids.

Results and Discussion

Permittivity models of the binary solvents

The real part ε' of the complex electric permittivity at 25 °C, 100MHz versus volume fraction were shown for the various binary mixtures (W-Et) and (Et-Mt) in Figure 1.

With an aim of finding a law of permittivity mixture which each studied binary composition obeys, we applied laws of mixtures [10 -12]. We deduce for the mixtures water-ethanol (W-Et), water-methanol (W-Mt) and ethanol-methanol (Et-Mt) the experimental values of the real part. For the mixtures water- ethanol (W-Et) and water- methanol (W-Mt) this behaviour agrees well with the Kraszewski Law given by:

$$\varepsilon_m = \left(\nu_1 \varepsilon_1^{1/2} + \nu_2 \varepsilon_2^{1/2} \right)^2 \qquad (1)$$

While for the mixture ethanol-methanol (Et-Mt) one, ε' versus volume fraction of methanol obeys to the Shivola-Kong Law:

$$\varepsilon_m = \varepsilon_2\left(1+\frac{(\varepsilon_1-\varepsilon_2)\upsilon_1}{\varepsilon_2+(\varepsilon_1-\varepsilon_2)(1-\upsilon_1)L_i}\right) \qquad (2)$$

Where:

ε_1 and υ_1 are respectively the relative permittivity and the volume fraction of liquid 1.

ε_2 and υ_2 are respectively the relative permittivity and the volume fraction of liquid 2.

L_i: depolarizing factor ($0< L_i<1$).

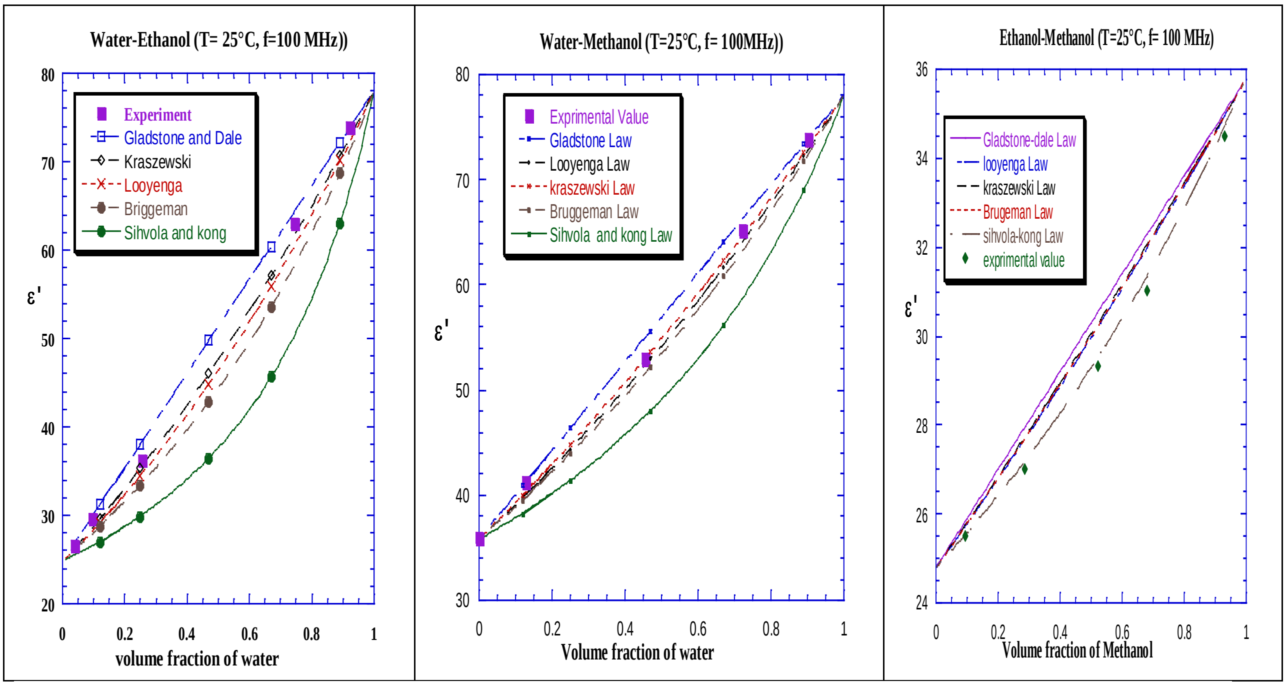


Figure 1: Real part ε' of the complex electric permittivity at 25 °C, 100MHz versus volume fraction for the various binary mixtures (W-Et), (W-Mt) and (Et-Mt).

Frequency dependencies of the complex Permittivities

Figures 2, 3 and 4 present the evolution of the real part ε' and the imaginary part ε” of the permittivity at 25 °C as function of to the frequency (noted f) respectively of the various compositions (W-Et), (W-Mt) and (Et-Mt). We notice that the values of the static dielectric constant, ε_s were obtained at the lowest frequency from the linear portion of ε'(ω), and are identified with the values of the real permittivity ε' [13]. In the same way we note, according to the curves of Figures 2 and 3, that the real part of the permittivity ε' and the maximum of the imaginary part ε''_{max} for the mixtures water-ethanol grow with increasing mole fraction of water. As shown in Figure 4, for the methanol-ethanol mixtures, the variation of ε' and ε''_{max} increases with increasing methanol concentration.

The increase in ε' can be explained by the raising in the total dipole moment, thanks to the interactions dipole-dipole, in the two systems studied following an additional portion of the made up one which presents the most raised permittivity; water for the mixture water-alcohol and methanol for the mixture alcohol-alcohol.

Moreover, in the field of studied frequency, water is a rather dissipative element of electromagnetic energy, that’s why increase in its mole fraction in the mixture involves a relative rise in the losses, which explains increasing in ε''_{max} of the environment. In the same way for the mixture alcohol-alcohol, methanol is more dissipative than ethanol for this reason the losses increase with increase mole fraction of methanol.

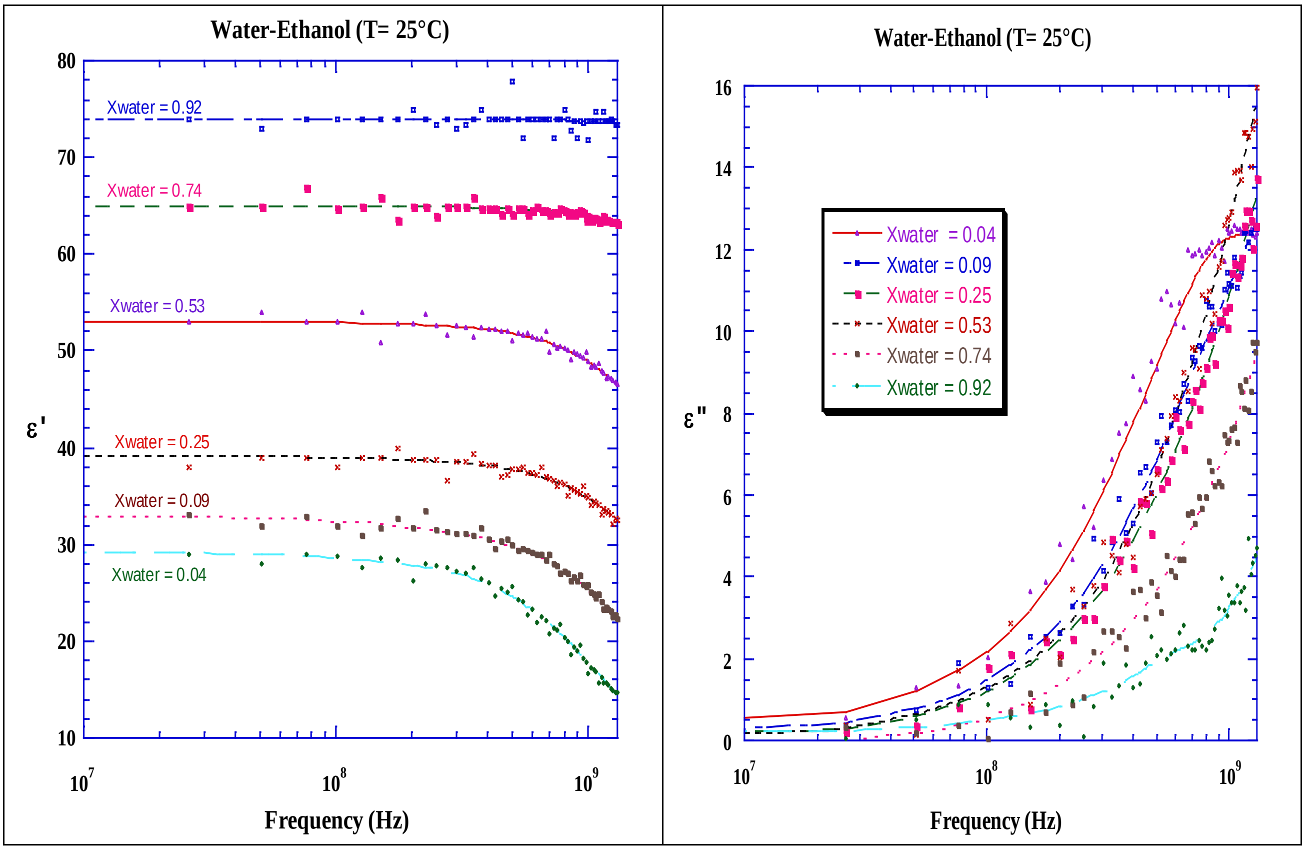


Figure 2: Dielectric spectra of Water-Ethanol mixture at 25 °C. (X is the mole fraction of water)

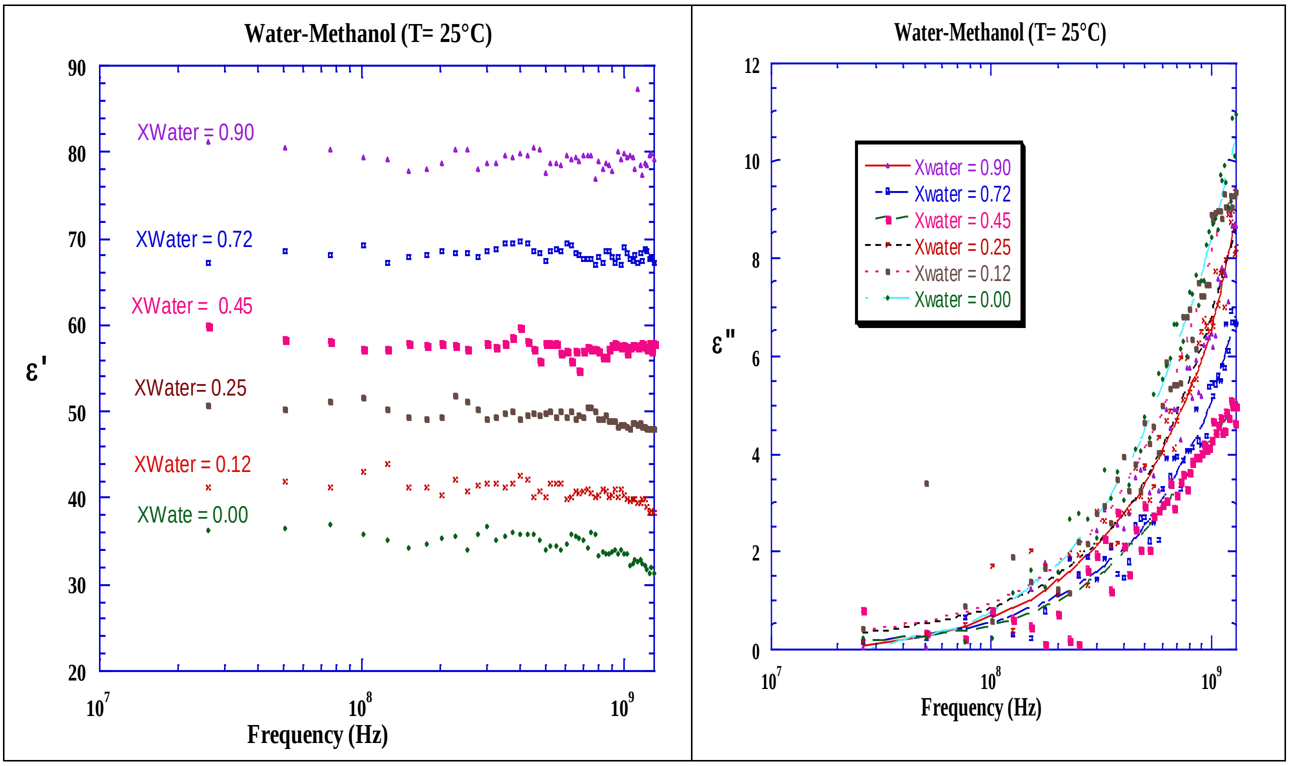


Figure 3: Dielectric spectra of Water-Methanol mixture at 25 °C. (X is the mole fraction of water).

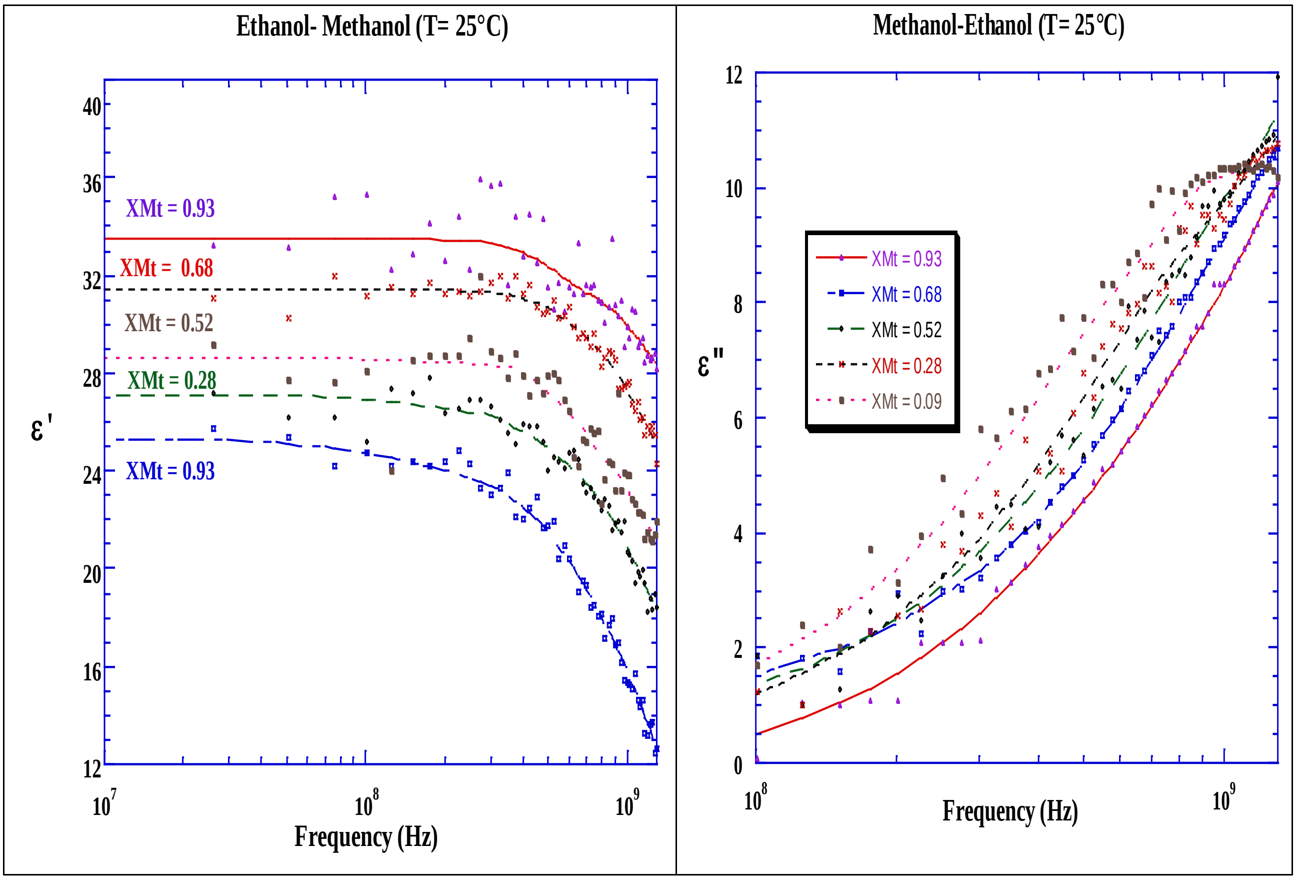


Figure 4: Dielectric spectra at 25 °C of binary mixtures Ethanol-Methanol (X is the mole fraction of methanol).

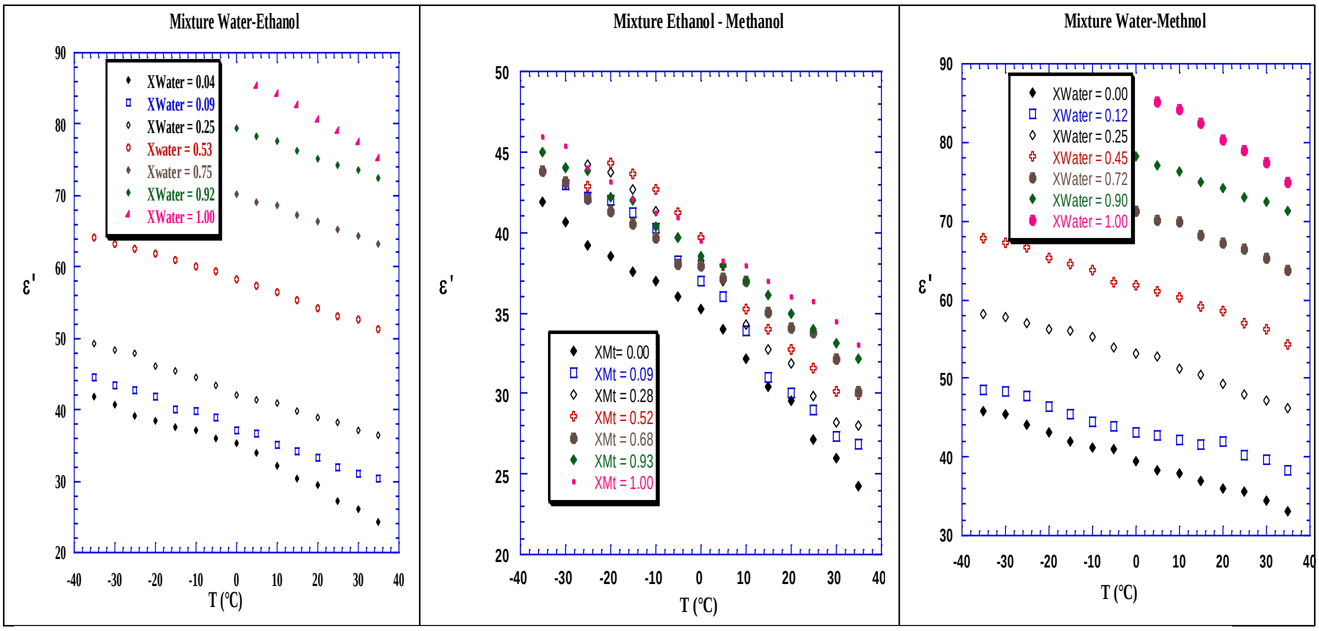


Figure 5: Real part ε' of the complex dielectric permittivity at 100MHz versus Temperature for the various binary mixtures (W-Et), (Et-Mt) and (W-Mt).

Temperature effects

The temperature is a very important factor of the dielectric properties because of its great influence on thermal agitation of the dipoles. In this part we have to vary the temperature of the mixtures from -35°C at 35°C. Figure 5 shows that the values of permittivity ε' of the mixture (W-Et), (W-Mt) and (Et-Mt) increases by decreasing the temperature. We can explain these variations of ε' by the fact that the principal interactions dipole- dipole which govern these mediums are due to the presence of the hydrogen bonds [7,13], these links have a weak dissociation energy, thus more one increases the temperature of the solution, one facilitates the rupture of these links what implies the reduction in the number of the electric dipoles in the solution and consequently a reduction in the permittivity.

Correlation with the Queen-King Law

With an aim of checking the validity of our measurements according to the temperature, we proceeded to a comparison between the experimental results and those given by the Queen-King Law. The expression Law giving the permittivity of binary mixture can be expressed by:

$$Log\varepsilon_{m,T} = \nu_1 Log\varepsilon_{1,T} + \nu_2 Log\varepsilon_{2,T} + \nu_1\nu_2 \sum_{j=0}^{2}\left[\frac{A_j(\nu_1-\nu_2)^j}{T}\right] \qquad (3)$$

We calculated the $A_{j(0\le j\le 2)}$ constants starting from three experimental points for water-alcohol mixtures and for methanol-ethanol mixture. Table 1 recapitulates our results found by calculation and those found in the literature [14]. We notice a good agreement between these values and we can affirm that our mixtures follow well the law of Queen-King.

Table 1: Comparison between experimental and literature $A_{j(0\le j\le 2)}$ constants mixture solvent.X* is the molar fraction of water for water-alcohol mixtures and of methanol for methanol-ethanol mixtures.

Mixture solvent	True X*	A_0(exp)	A_0(liter)	A_1(exp)	A_1(liter)	A_2(exp)	A_2(liter)
Water-Methanol	0.53	188.3	181.0	32.5	33.3	-16.3	-16.9
Water-Ethanol	0.45	247.5	246.8	23.8	22.1	-55.8	-51.5
Methanol-Ethanol	0.52	102.3	----	25.9	----	-12.1	----

Relaxation and time relaxation study

Water interacts strongly with alcohols through on hydrogen bonded clusters and cooperative process for the molecules. Water, ethanol and methanol are hydrogen bonded liquids and completely miscible with each other and each of them exhibits a principal dispersion of the Debye or near Debye type in the microwave frequency range. The mechanism for this dispersion is suggested to be rotational diffusion of the polar molecules or their clusters.

The dielectric relaxation behaviour of the mixtures can be associated to the relaxation mechanism of the pure solvents however the magnitude of the principal relaxation time τ and amplitude of each relaxation process could be related to the temperature and the composition of mixtures solvent.

Water-Ethanol mixture, for selected mole fractions at 25 °C, can be described better with a Cole-Davidson function as shown with the Cole-Cole diagram illustrated in Figure 6.

For the methanol-ethanol mixtures a Debye function gives a good fit for frequency below 1.3 GHz, besides the pure methanol and ethanol liquids show similar behaviour (Debye type) to that of ethanol-methanol mixtures, as shown in Figure 7. This result has been suggested that the two different alcohol molecules may behave interchangeably in forming intermolecular clusters and that the mechanisms of the dielectric relaxation for the pure alcohols and their mixture are the same [15].

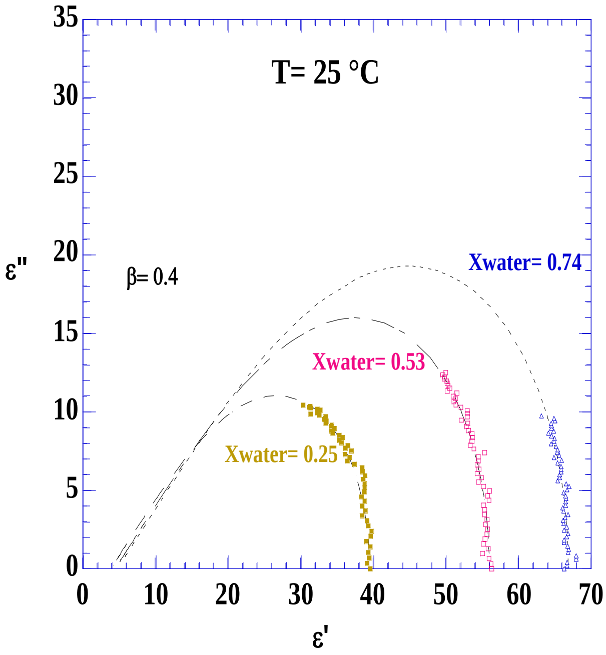


Figure 6: Cole-Cole diagram for water-ethanol mixture at 25 °C

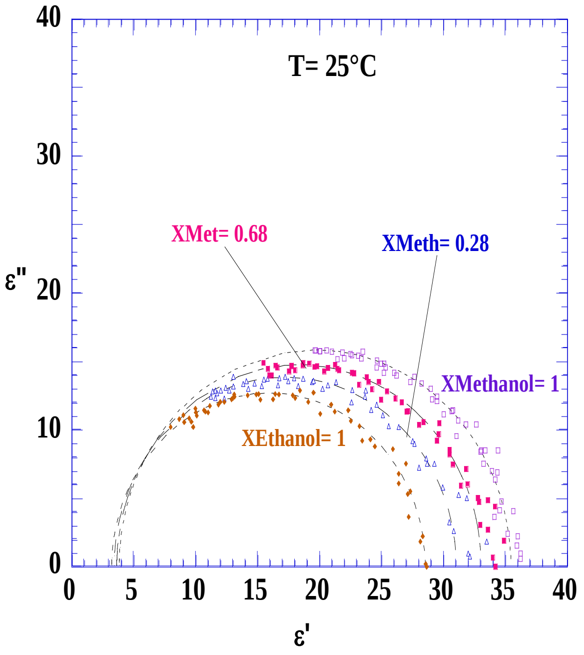
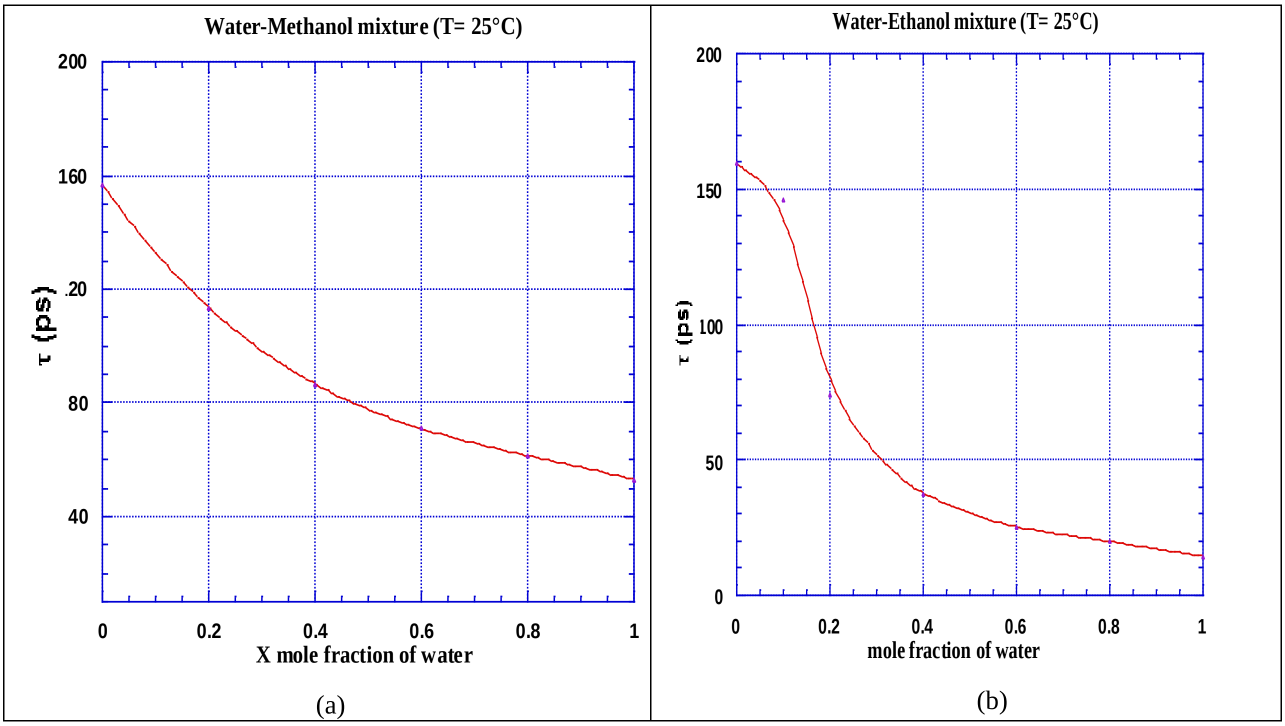


Figure 7: Cole-Cole diagram for pure methanol, ethanol and their mixture at 25 ° C

The relaxation time τ, describes the time necessary of the dipoles to relax under the given conditions. Several theories [1,5,9,16] were proposed to explain the relaxation mechanism of the mixtures water alcohol. One of these theories was established by Bertoloni, Cassetari and Salveti which consider that the relaxation time is governed by two times τ1 and τ2. The first time τ1 is allotted to the relaxation of the mobile or free fraction of the solution made up of monomers. The second time τ2 relating to the relaxation of the motionless fraction of the solution consists of alcohol and water molecules bound by hydrogen bonds. Mobile fraction lines up more quickly with the direction of the electric field applied, therefore has a relaxation time weaker than that of the motionless fraction which requires a larger time for the reorganization of its network. In our work we can observe only one relaxation timeτ, considering our field of frequency is limited to a 1.3GHz. The τ values were plotted in Figures 8-a and 8-b against the mole fraction of water in the water-alcohol mixtures. As it can be seen from these figures, the relaxation time τ in the aqueous mixtures sharply increased with increasing alcohol concentration. The common interpretation consists of invoking that water is a high dispersing solvent. Water is able thanks to the interactions dipoles-dipoles to maintain the alcohol molecules in a state of dispersion and consequently confers better mobility of these molecules.



(a) (b)

Figure 8: Relaxation time of (a) water-methanol and (b) water-ethanol mixtures at 2

Conclusion

In this paper we have reported the results of dielectric properties for water-ethanol, water-methanol and methanol-ethanol binary mixture solutions in the frequency range 10^7 to 1,3 10^9 Hz. We have observed for the real part ε' of the permittivity of the binary water-alcohol mixture a behaviour that agrees well with the Kraszewski Law and for the mixture ethanol-methanol ε' can be fitted according to the Shivola-Kong Law. Correlations are provided that precisely describe the permittivity with composition and its frequency dependence. A remarkable change of dielectric constant of water-alcohol and alcohol-alcohol mixtures coupling temperature is observed with change of composition and frequency. The validity of permittivity measurements according to the temperature are verified by the Queen-King Law and the $A_{j(0\leq j\leq 2)}$ constants are compared with literature data.

The dielectric relaxation is observed for the mixtures and can be associated to the relaxation mechanism of the pure solvents. The magnitudes of the principal relaxation time τ and amplitude of each relaxation process as functions of the concentration mixture have been obtained.

Experimental Section

Solution preparation

Solutions of the various mixtures were prepared using bidistilled water (W), ethanol (Et) from Panreac Quimica and the pure methanol (Mt) supplied by Biothechnica.

Water-Ethanol (W-Et), water-methanol (W-Mt) and ethanol-methanol (Et-Mt) solutions were prepared by weighing using a balance of precision 0.1 mg and by agitating the mixtures during 15 min in order to homogenize them.

Different water-alcohol and alcohol-alcohol proportions were employed molar fraction ranging from 0 to 1.

Dielectric measurements

The dielectric measurements were carried out with a HP 8712ES vector network analyzer with an electromagnetic source which works over the frequency range of [300 kHz, 1.3 GHz]. An open-ended coaxial line probe with 3.5 mm diameter was connected to it[17-18]. The open side of the coaxial probe (cable: coaxial waveguide) is put in contact with the liquid mixture, as shown in Figure 9.

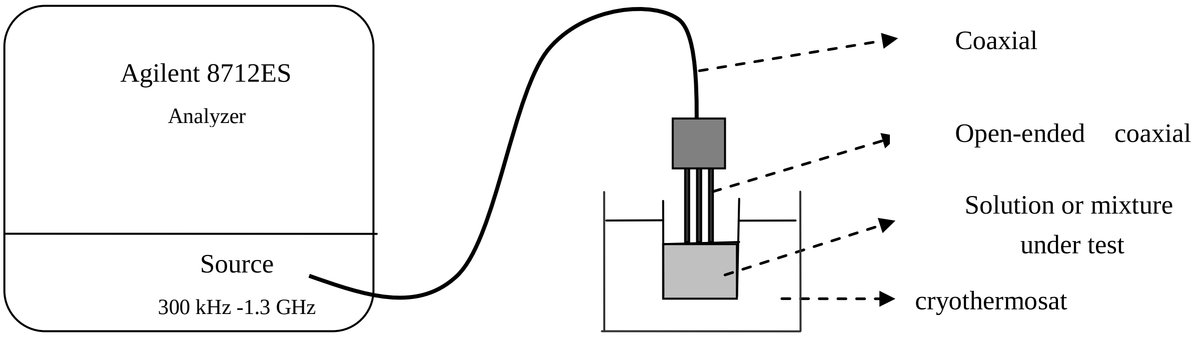


Figure 9: Open-ended coaxial line set-up connected to a network analyzer

The calculation of the complex permittivity is determined from the measurements of the complex reflection coefficient S_{11} of the guided electromagnetic wave as reported in equation (1)[19].

$$S_{11} = \text{Reflected wave / Incident wave}$$
$$= (1-j\omega C_0 Z_0\, \varepsilon^b) / (1 + j\omega C_0 Z_0\, \varepsilon^b)^* (1+ j\omega C_0 Z_0) / (1 - j\omega C_0 Z_0) \quad (1)$$

Where ω is the angular frequency of the electromagnetic wave; C_0 and b are the open-ended coaxial line parameters; Z_0 is the characteristic impedance of the coaxial line; ε permittivity of the dispersion under test.

For the temperature measurements, the Cryothermostat Julabo FP 40-HE controlled water bath was used. It allows the automatic adjustment of the temperature. This apparatus is equipped with a thermostat, which stabilizes the temperature of the bath in which the sample is introduced, within a range of [- 35 °C, + 35 °C].

When the set temperature was reached, the open ended coaxial probe was put in contact with the dispersion. Then data of the complex reflection coefficient S_{11} were collected over the set frequency range [10 MHz, 1.3 GHz]. The estimated uncertainty for the real part of the determined complex permittivity was in the order of 5%. The best measurements accuracy and resolution were achieved around the centre.

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