Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi
Afyon Kocatepe University – Journal of Science and Engineering
https://dergipark.org.tr/tr/pub/akufemubid

Araştırma Makalesi / Research Article
DOI: https://doi.org/10.35414/akufemubid.1363525
AKÜ FEMÜBİD **24** (2024) 021101 (255-259)
AKU J. Sci. Eng. **24** (2024) 021101 (255-259)

Investigation of Dielectric Constants of Alcohol-Water Mixtures by Microwave (MW) Spectroscopy Technique

Makale Bilgisi / Article Info
Alındı/Received: 20.09.2023
Kabul/Accepted: 07.03.2024
Yayımlandı/Published: 29.04.2024

Alkol-Su Karışımlarının Dielektrik Sabitlerinin Mikrodalga (MD) Spektroskopi Tekniği ile İncelenmesi

Cengiz OKAY*
Marmara University, Faculty of Science, Department of Physics , İstanbul, Türkiye

Öz

Son birkaç on yılda, endüstride mikrodalga (MW) spektroskopi uygulamalarının kullanımı önemli ölçüde artmıştır. Bu teknik, dielektrik parametrelerin (Ɛ' ve Ɛ") ölçümü yoluyla alkol-su karışımları hakkında çok önemli ayrıntılar vermesi nedeniyle oldukça kullanışlıdır. Bu çalışmada, saf sudan saf alkole doğru konsantrasyon değişimleri için etanol-su ve metanol-su karışımlarının dielektrik parametreleri (Ɛ' ve Ɛ") belirlendi. Etanol-su ve metanol-su karışımlarının dielektrik parametrelerinin (Ɛ' ve Ɛ") kırılma noktalarının %43 ve %44 hacim fraksiyonlarında, x_{et}≈ 0.20M ve x_{met} ≈ 0.26M molar fraksiyonlarında olduğu tespit edildi.

Anahtar Kelimeler: *Mikrodalga tekniği; Dielektrik parametre; Permittivity; Alkol-su karışımları*

Abstract

Over the last few decades, the utilization of microwave (MW) spectroscopy applications in industry has grown dramatically. This technique is very useful as it gives very important details about alcohol-water mixtures through the measurement of dielectric parameters (Ɛ' and Ɛ"). This research determined the dielectric parameters (Ɛ' and Ɛ") of ethanol-water and methanol-water mixtures for concentration changes from pure water to pure alcohol. The ethanol-water and methanol-water mixture volume fractions of 43% and 44%, respectively, as well as the molar fractions x_{et}≈ 0.20M and x_{met} ≈ 0.26M, obtained the breaking points of the dielectric parameters (Ɛ' and Ɛ").

Keywords: *Microwave technique; Dielectric parameter; Permittivity; Alcohol-water mixtures*

1. Introduction

Many industrial applications involve using ethanol and other alcohols, as well as their aqueous water mixtures. Ethanol and methanol are the most often utilized alcohols when water is dissolved at room temperature. Alcohol' heterogeneity, which results from the development of alcohol-alcohol, water-water, or alcohol-water clusters, is a crucial characteristic. Alcohol-water binary combinations have already been thoroughly researched using a variety of techniques, such as molecular dynamics simulations (MDS) (Benmore and Loh 2000, Tanaka et al. 1985), X-ray scattering (Hayashi et al. 1990, Nishikawa and Lijima 1993), mass spectroscopy (Takamuku et al. 2000), nuclear magnetic resonance with time domain (TD-NMR) technique (Jora et al. 2017, Okay 2023, Yoshida et al. 2006), Microwave dielectric spectroscopy (Kanse et al. 2006, Mohsen-Nia et al. 2010, Morlyoshl et al. 1990, Oğuzhan Akgöl 2020). Due to its remarkable sensitivity to molecule polarization or collective dynamics, dielectric spectroscopy (DS) is thought to be one of the most attractive techniques for investigating the unique structures of water clusters and alcohol structures. One important physicochemical property of a solvent is its dielectric constant. Dielectric constants have important scientific and biological applications. A charged particle's dielectric constant tells us how strong the electric field is around it in a solvent (Mohsen-Nia et al. 2010). Permittivity is a measure of a material's dielectric properties. The dielectric loss factor on the imaginary part of the permittivity constant's Ɛ" real portion is referred to as Ɛ'. The material's dielectric constant (Ɛ') indicates how much energy it can hold, and the dielectric loss factor (Ɛ") indicates how much energy is created by the material. It claims that it can take in energy and turn it into heat (McSweeney and B. P. L. H 1995, Tataroğlu 2013).

In this study, the permittivity constants Ɛ' and Ɛ" known as dielectric parameters of the ethanol-water and methanol-water mixture have been investigated from pure water to pure alcohol. The dielectric behavior of alcohol-water mixtures is explored using the hydrogen-bonded hypothesis.

*Sorumlu Yazar/Corresponding Author: Cengiz OKAY e-posta/e-mail: cokay@marmara.edu.tr

2. Materials and Methods

2.1. Experimental Procedures

The liquid forms of methanol and ethanol were purchased from Sigma-Aldrich® (99%). Deionized water (Milli-Q, 18.2 M) with various volumes and molar fractions was used to create a mixture of ethanol and methanol that was also maintained at room temperature. Agilent Technologies' E8364B PNA series network analyzer (VNA) and Agilent 85070E Dielectric Slimform Probe Kit were used to measure a set of samples with varied alcohol concentrations in alcohol-water combinations (**Figure 1**). A 50-ohm load terminal, pure water, and air at 25 °C were used to calibrate the liquid test fixture. Alcohol-water mixture samples were measured at 25 °C in a frequency range of 10 MHz to 50 GHz.

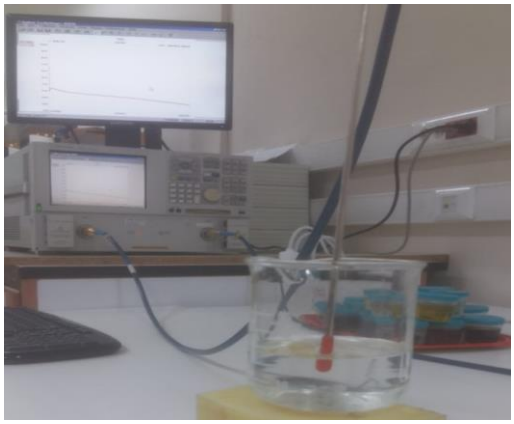

Figure 1. Photo of Agilent Network Analyzer (VNA) and Dielectric Kit.

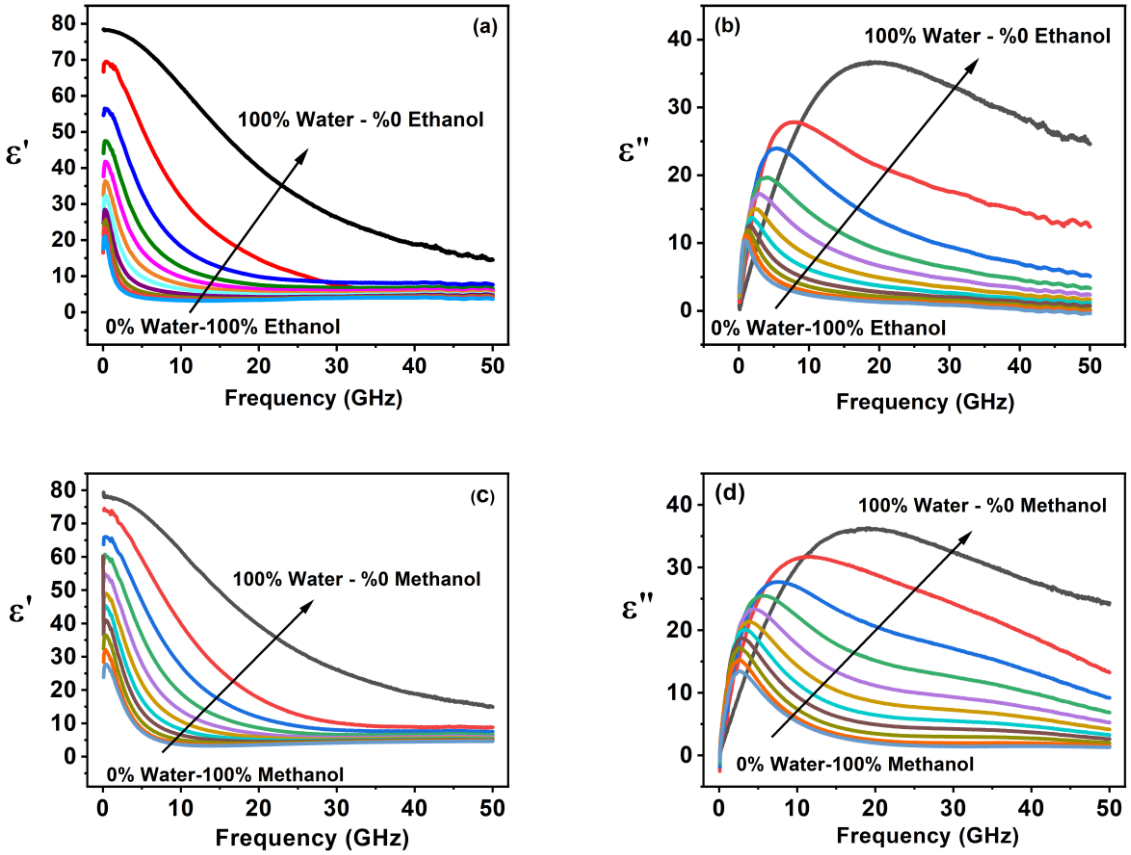

Figure 2.a-d. Real and imaginary parts of dielectric spectra of ethanol-water, and methanol-water mixtures (molar fractions at 25 °C).

3. Results and Discussions

Figure 2. a-b-c-d. displays the dielectric constants (Ɛ' and Ɛ") spectra of the two types of alcohol-water mixture from pure alcohol to pure water—ethanol-water and methanol-water (molar fractions)—as a function of frequency, from 10 MHz to 50 GHz. At least three repeats of each measurement were performed. The measurements of the dielectric constant Ɛ' and Ɛ" were taken as the average value (at 1 GHz). The obtained dielectric constants (Ɛ' and Ɛ") from pure water to pure alcohol (volume and molar fractions) are displayed in Figures 3. a–b and Figures 4. a–b, respectively. The figures demonstrate that for all of the investigated aqueous solutions, the dielectric constant values (Ɛ') dropped as the concentrations of methanol and ethanol increased. In addition, the results show that for all of the aqueous solutions under investigation, the dielectric constant values (Ɛ") rose as the concentrations of methanol and ethanol increased. The trends in the Ɛ' and Ɛ" values for varied amounts of water-methanol and water-ethanol combinations (Figures 3 and 4) are similar. After the

measurements were made, the dielectric constant was compared to values reported in the literature, which demonstrated the accuracy of the data (Kanse et al. 2006, Lone et al. 2008, Mohsen-Nia et al. 2010). When comparing my findings to the values reported in the literature, the margin of error for the dielectric measurements of pure water, methanol, and ethanol was roughly 2,4%, 10%, and 38%, respectively. It is clear that the outcomes produced by the commercial Agilent 85070E Dielectric Slimform Probe Kit and Agilent E8364B PNA series network analyzer devices are in agreement with one another.

Returning to Figures 3 and 4, the results show that the Ɛ' values for methanol-water mixtures are consistently higher than those for ethanol-water mixtures. Physical properties of compounds, such as solubility, melting and boiling points, and intermolecular interactions, are correlated with their molecular polarity. It is known how the polarity of the molecule and the dielectric constants relate to each other. Additionally, molecules that possess O-H bonds have the ability to form hydrogen bonds. As the length of an alcohol's alkyl chain increases, London dispersion forces between molecules can increase and even surpass (as in the case of ethanol). Consequently, methanol displays a minimal London dispersion force, and its reported dielectric constants are greater than ethanol's, as expected (Kanse et al. 2006, Lone et al. 2008, Mohsen-Nia et al. 2010).

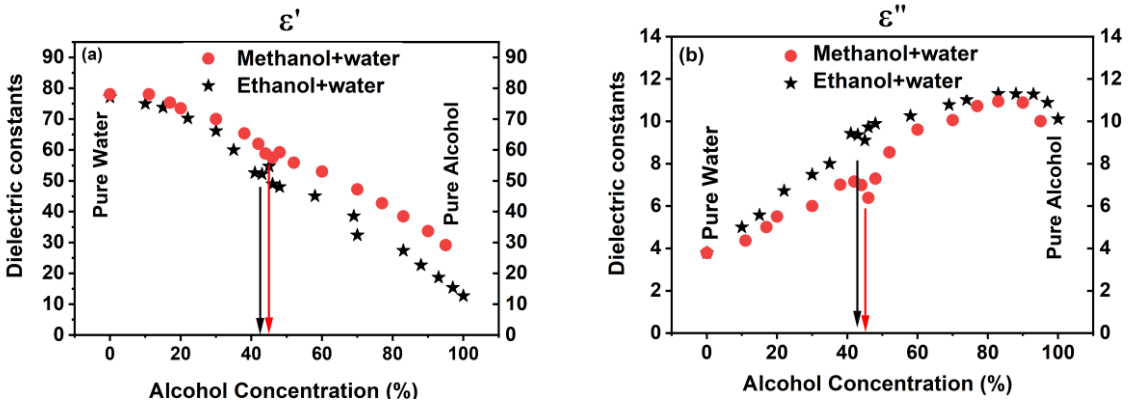

Figure 3. a–b Dielectric constants (at 1 GHz) ethanol-water and methanol-water for volume fraction

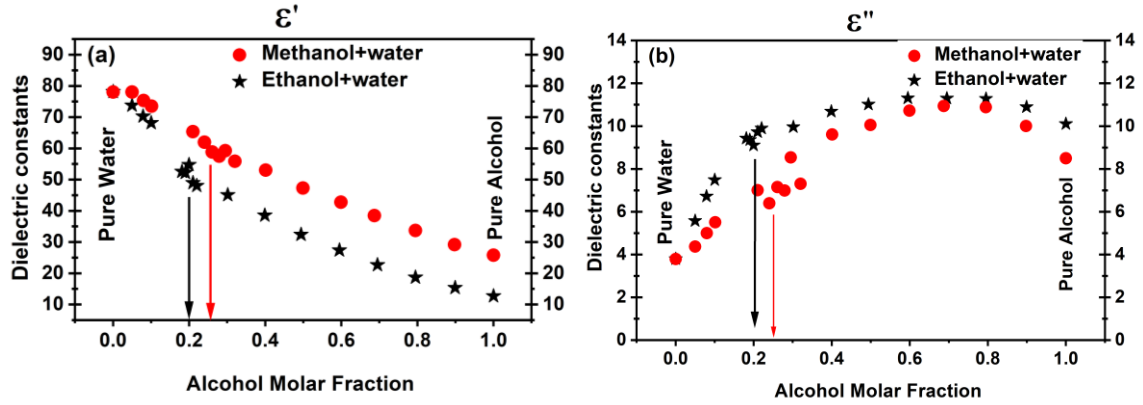

Figure 4. a–b Dielectric constants (at 1 GHz) ethanol-water and methanol-water for molar fraction

As we previously stated, both types of alcohol show a fairly similar tendency in the dependence of Ɛ' and Ɛ" vs. concentration. The only difference between ethanol-water and methanol-water mixture is the values of the turnover (breaking) points. Arrows are provided as references to indicate certain volumes-molar fraction (breaking) points in the Ɛ' and Ɛ" values. Arrows are provided as a guide to indicate special volume concentrations; they read 43% for ethanol and 44% for methanol. These values correspond to $x_{et} \approx 0.20$ and $x_{met} \approx 0.26$ in the molar fractions of ethanol and methanol-water mixes, respectively. Ɛ' decreases with the increase of concentration toward turnover points. Following that, Ɛ' values rise and subsequently fall with larger alcohol fractions in the direction of pure alcohol liquid. Similarly, Ɛ" rises as alcohol content increases approaches turnover points. After that, Ɛ" values decline and then increase with larger alcohol fractions toward pure alcohol liquid.

The alteration in the alcohol-water clusters' transition structure is connected to this breaking point. Additionally, it is reliant on the forming of hydrogen bonds between molecules of alcohol and water. The rotational and translational motion of water and molecules are also impacted by this clumping phenomenon. Several research teams (Burikov et al. 2010, Matsugami et al. 2016, Takamuku et al. 2001, 2004) have used a variety of methodologies to examine the hydrogen-bonding characteristics of the alcohol-water system. We provided the following explanation for the observed concentration

dependence using information from the literature. It is well known that pure water molecules, even when they are in a liquid condition, prefer a tetrahedral arrangement. This means that, on average, neighboring molecules are orientated to one another so that they create water clusters that are tetrahedral for a brief period (in the near range). A small amount of alcohol does not immediately change this dynamic organization, but as the alcohol concentration rises, the water molecules' near-range arrangement begins to change. At volume concentrations of %43 (x_{et}≈ 0.20M) for ethanol and %44 to (x_{met} ≈ 0.26M) for methanol, the tetrahedral-like organization breaks down in the intermediate concentration range because alcohol-water clusters rather than water-water clusters occur in the mixes. An increase in the number of chain-like clusters of alcohol molecules and a drop in the ratio of alcohol-water clusters are the effects of raising the alcohol concentration above turnover concentrations (Noskov et al. 2005, Takamuku et al. 2000, Yoshida et al. 2006).

4. Conclusions

In this study, the dielectric parameters (Ɛ' and Ɛ") of ethanol-water and methanol-water mixtures from pure water to pure alcohol (volume and molar fractions) have been examined using the microwave (MW) spectroscopy technique. Both types of alcohol showed the same tendency in terms of how concentration affects dielectric parameters. Ɛ' decreased as concentration increased approaches turnover points. Following that, Ɛ' values raised and then fell with increasing alcohol fractions in the direction of pure alcohol liquid. Similarly, Ɛ" climbed as alcohol content reached turnover points. After that, Ɛ" values decreased and subsequently increased with increasing alcohol fractions toward pure alcohol liquid. The observed behavior is qualitatively explained.

Declaration of Ethical Standards

The author declares that they comply with all ethical standards.

Credit Authorship Contribution Statement

Author: Conceptualization, investigation, methodology and software, supervision, visualization, and writing – original draft, review, and editing.

Declaration of Competing Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The author declares that the main data supporting the findings of this work are available within the article.

Acknowledgement

I would like to thank Prof. Dr. Bulat Rami and Dr. Ayşe Maraşlı from Gebze Technical University for providing laboratory facilities and access to equipment.

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