RASĀYAN *J. Chem.*
Vol. 18 | No. 4 |2165-2171| October-December | 2025
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

DIELECTRIC RESPONSE OF NON-ARRHENIUS WATER CONTAINED/ACCOMMODATED IN MCM-41 AND MCM-48 SILICATES: A TEMPERATURE–DEPENDENT PHASE TRANSITIONS STUDY

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ABSTRACT

Water has an anomalous property. In fact, this is the only one that exists in all 3 states of matter. Water with zeolite bed of Silica matrices of mesoporous Nano channels of MCM-41 and MCM-48 were kept in pore diameters of size 2.2, 2.5, and 2.7 nm, with a varying temperature range of 80K to 300 K, utilizing a frequency range of 1 MHz to 20 Hz. Dielectric studies revealed that different relaxation peaks were found in all pore diameters with respect to temperature and measurement frequency, but an exceptional and huge dielectric content of ε' ~ 104 was found at 2.7 nm. It indicates that the pore diameter had a significant bump in the dielectric response. A pore-size-independent dielectric relaxation was seen at lower temperatures (160–220 K), exhibiting properties similar to thermally activated relaxation in bulk ice. The high temperature relaxation (230-280K) exhibits a non–Arrhenius pore type behaviour with pore size> 2.5 nm.

Keywords: Mesoporous Materials, Confined Water, Non-Arrhenius Behavior, Dielectric Characteristics, Dielectric Relaxation, Pore Size's Impact Change.

RASĀYAN *J. Chem.*, Vol. 18, No. 4, 2025

INTRODUCTION

Water's unusual temperature-dependent behaviour in both liquid and supercooled states has sparked a lot of interest in recent studies of its structural and kinetic characteristics.[1,2] Strong hydrogen bonds between water molecules are the main cause of these anomalies. A variety of experimental methods, such as neutron diffraction[2], calorimetry[3–9], and nuclear magnetic resonance (NMR) spectroscopy[15], have been used to investigate water confined within nano-porous materials like porous silica in order to gain a better understanding of these behaviours. According to these investigations, the pores contain three different types of water: (i) free or core water at the centre, (ii) bound or shell water next to the pore walls, and (iii) an intermediate layer in between the bound phase transitions. These techniques include NMR spectroscopy, neutron diffraction,[2] calorimetry. These studies revealed a variety of water molecules in the pores, such as free or core water in the middle of the pores, bound or shell water adjacent to the pore walls, and an intermediate layer between these effects. At lower temperatures, bound water freezes and melts considerably more slowly than free water.[10,11] As it cools, the bound water continuously changes from a two to a more rigid structure.[11] Free water freezes below the bulk freezing temperature as the temperature drops, and its structure is remarkably similar to that of bulk water. These techniques include NMR spectroscopy[15], calorimetry[3–9], and neutron diffraction.[2] These studies demonstrated the existence of different kinds of water molecules inside the pores, including bound or shell water close to the pore walls, free or core water in the middle of the pores, and an intermediate layer between these two areas. Compared to free water, bound water freezes and melts much more slowly and at much lower temperatures.[10,11] As the temperature decreases, bound water gradually becomes more rigid.[11] In contrast,

http://doi.org/10.31788/RJC.2025.1849319

free water freezes below the bulk freezing point and shares a structure with bulk water. Free water exhibits strong hysteresis during thermal cycling and melts at temperatures higher than its freezing point.[8,11,13] However, when water adopts the crystalline structure of ice, this hysteresis is not seen. The absence of well-characterized materials with precisely defined pore structures is one of the main obstacles to studying confined water, and it frequently makes it more difficult to interpret experimental data. The siliceous material MCM-41 has the most consistent one-dimensional pore architecture among different porous silica matrices. It provides the capacity to host guest species, a wide surface area, and a narrow distribution of pore sizes. They can accommodate guest species; have a large surface area, and a very limited range of pore sizes. XRD,[5,6,7] neutron scattering,[7] isothermal adsorption,[8] and 1H nuclear magnetic resonance (NMR) studies[14,15] have looked at Water adsorption in mesoporous MCM-41 with varying pore sizes, demonstrating unique physical properties shaped by confinement effects. Physical characteristics of water adsorbed in mesoporous MCM-41 materials with varying pore diameters. The results show that the pores contain two different kinds of water. While the second phase of the water gradually freezes at lower temperatures in a glass-like manner, in its initial phase, confined water freezes into a cubic ice structure, while free water occupies the central regions of the pores. A physical property of water adsorbed in mesoporous MCM-41 materials with different pore diameters has been examined in[14,15] studies. The findings indicate that there are two types of water present in the pores. The first phase of the water exhibits an initial phase that demonstrates standard freezing into a cubic ice structure resulting from confinement, with free water present in the pore core; conversely, the subsequent phase undergoes progressive freezing as the temperature declines in a glass-like manner. Despite a great deal of research, many questions remain. For instance, there is a debate over the dynamics of supercooled water. Many basic questions concerning the behaviour of confined water remain unanswered despite a great deal of research. The dynamics of supercooled water, for example, are still up for discussion. Proton transfers between hydrogen-bonded water molecules and the water's large dipole moment have a major impact on the structural and dynamical characteristics of water trapped in one-dimensional (1D) Nano channels. Since molecular motion directly affects the relaxation of dielectric polarization, dielectric spectroscopy−which is sensitive to molecular orientation−offers important insights into these dynamics. Measurements of relaxation rate can be used to quantitatively evaluate the reorientation kinetics of water molecules. A recent study applied dielectric spectroscopy to examine the molecular dynamics of water confined within MCM-41 mesoporous structures.to explore the dynamics of water confined in MCM-41 Nano channels. Observations indicate that bound and free water exhibit different structural behaviours, such as temperature-dependent phase transitions and strong hysteresis. Measurements of dielectric relaxation verified that confinement has a significant impact on dipole reorientation and molecular mobility.

EXPERIMENITAL

Capacitance (C) and dielectric loss tangent (tan δ) were measured between 80 K and 350 K across frequencies from 20 Hz to 1 MHz, utilizing an HP-4284A LCR meter and a computer-controlled Lakeshore temperature controller. The round, dish-shaped samples have dimensions of 10 mm in diameter and 1 mm in thickness. The two sides covered in silver paint served as the electrodes for the measurements. The sample was first cooled to 80 K, and then it was heated from 80 K to 350 K in steps of 5 K in order to complete the measurements. During the frequency scan, the temperature was within 0.2 K of the set point, and evacuation is still ongoing to prevent condensation. The complex dielectric constant, comprising its real (ε′) and imaginary (ε″) components, was calculated from the raw data and the sample's geometric parameters. The formulas $\varepsilon' = C\,d / \varepsilon_0 A$ and $\varepsilon'' = \varepsilon' \tan\delta$, where d is the sample thickness, A is the cross-sectional area, and ε0 is the permittivity of free space, were used to determine the real (ε') and imaginary (ε") components of the complex dielectric constant (ε*).

RESULTS AND DISCUSSION

Plotting the powder diffraction data scattering intensity against the scattering angle 2θ resulted in a diffractogram. Figure-1 displays the synthesised MCM-41 powders' small-angle XRD patterns. Visibly visible are three distinct peaks, represented by the indices (1 0 0), (1 1 0), linked to two-dimensional hexagonal symmetry (p6 mm).[9] Please display a few pertinent papers. Figure-2 illustrates how the

nitrogen adsorption studies can be used to ascertain the assessment of the mesoporous framework, depending on specific surface area and pore size distribution as essential parameters of MCM-41. The amount and pressure of nitrogen gas adsorbed on the sample surfaces were compared using this technique. Typically, the Brunauer-Emmett-Teller (BET) model is used to analyze the nitrogen adsorption isotherm obtained from this.[11] The BET surface area of MCM-41 was approximately 1,148 m^2/g.

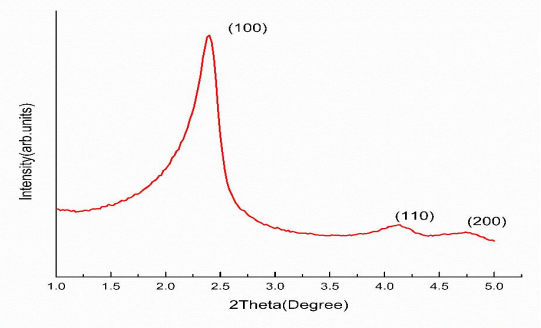

Fig.-1: XRD Pattern of MCM41

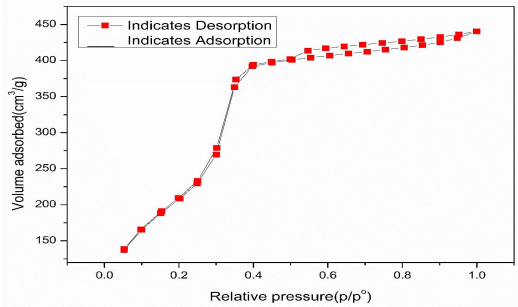

Fig.-2: Absorption of Nitrogen Studies of MCM41

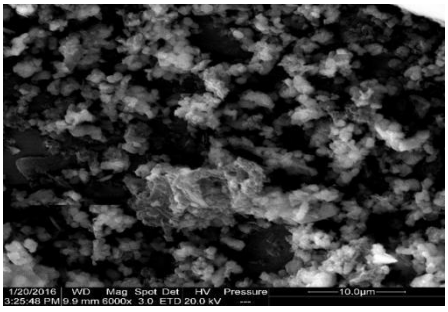

Fig.-3: SEM image of MCM41

Figure-3 shows that the substance's structure is very porous, with randomly formed holes and networks with connections, perfect for experiments in limited water. There are several bigger clusters that may be seen, which could be areas where different confinement sizes could cause different water relaxation. The distinct limits of the Nano channels indicate possible molecular interaction paths.

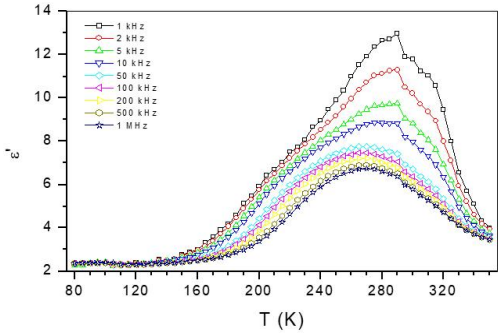

Fig.-4a: S'(T) Shows a Constant Value of Around 3 Below 160 K

Figure-4a reveals that for water confined in 2.7 nm holes at different test frequencies, the relationship between temperature and the real component of dielectric permittivity (s') is shown in Fig.-4a. S'(T) shows a constant value of around 3 below 160 K, regardless of frequency or temperature. The dielectric permittivity is strong at room temperature (s' ~ 6 x 10^3 for 1 kHz), and the s'(T) curves show two different transitions below room temperature. Water in nanopores has a s' value of about 90 at 273 K, which is significantly different from that of bulk water (Neagu et al., 2000). The loss tangent (tanδ) data for water in 2.7 nm holes at certain frequencies, which fluctuates with temperature, as illustrated in Fig.-4b.

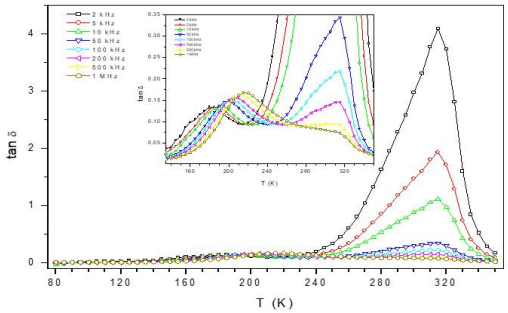

Fig.-4b: The Loss Tangent (tanδ) Data for Water in 2.7 nm Holes

The AC conductivity (σ_a) of water contained in 2.7 nm pores changes with frequency (f) at various temperatures, as shown in Fig.-5.

Two separate regions can be seen in the σ_a(f) curves: Low-frequency region: As frequency increases in this range, conductivity noticeably increases. The grain boundaries' blocking effect, which obstructs charge carrier motion, is responsible for this behavior. At lower frequencies, polarization builds up and conductivity increases more sharply because ion movement is impeded at interfaces like pore walls or grain boundaries. The rate at which conductivity increases slows down in the high-frequency region. The Universal Dielectric Response (UDR), which represents the relaxation of bulk conductivity processes, is frequently used to characterize this phenomenon. In this regime, interfacial effects do not substantially impede charge carriers' ability to react to the applied field. A helpful framework for deciphering the high-frequency dielectric response of confined water is provided by the UDR model. The confinement inside nanopores changes the dynamics of charge transport and polarization, affecting both electrical and dielectric responses, in contrast to bulk water. This work advances our knowledge of how water's electrical behavior is drastically altered when constrained in nanoscale environments compared to its bulk phase behavior.

Figure-6 shows the Behaviour of Dielectric Permittivity in Confined Water. Water's dielectric response varies significantly with temperature and frequency, suggesting a variety of polarization mechanisms contained in nanopores. To assess the effect of confinement, water confined in MCM-41 with pore diameters of 2.7 nm, 2.5 nm, and 2.2 nm was examined. To evaluate the impact of pore size on dielectric behavior, measurements were made of the loss tangent (tan δ) and the real dielectric permittivity (ε′) and loss tangent (tan δ) were analyzed to determine their dependence on frequency and temperature (s') show notable departures from the behaviour of bulk water, indicating intricate relaxation dynamics in the restricted space.

Behaviour of Dielectrics at Low Temperatures

Below 160 K, pore diameters for all investigated are mostly unaffected by temperature or frequency. Approximately 5 for 2.7 nm holes, ~2.5 for 2.5 nm pores, and a comparable number for 2.2 nm pores are the intrinsic static dielectric constant values, which decrease with decreasing pore size. This pattern implies that confinement effects, which are probably caused by decreased molecular mobility and modified hydrogen bonding networks at low temperatures, dramatically change the static dielectric response.

Figure-7 shows two step-like rises at higher temperatures, which line up with the tan curve peaks. The existence of discrete relaxation processes connected to the molecular dynamics of confined water is

indicated by these transitions. The significant influence of nano confinement on the dielectric characteristics of water is further shown by the high dielectric permittivity values measured at room temperature (for 2.7 nm holes at 1 kHz). The dielectric permittivity at room temperature is almost six times lower for 2.5 nm pores than for 2.7 nm pores, and its magnitude diminishes as the pore size decreases. At ambient temperature, there is a noticeable drop to about 12.5 for 2.2 nm pores. Variations in the dynamics of water molecules, hydrogen bonding interactions, and ice-like ordering inside the restricted regions are the causes of these discrepancies.

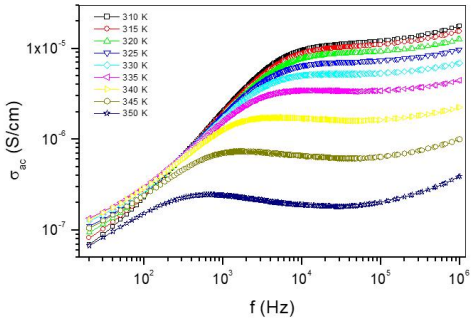

Fig.-5: The AC Conductivity (σAC) of Water is Contained in 2.7 nm.

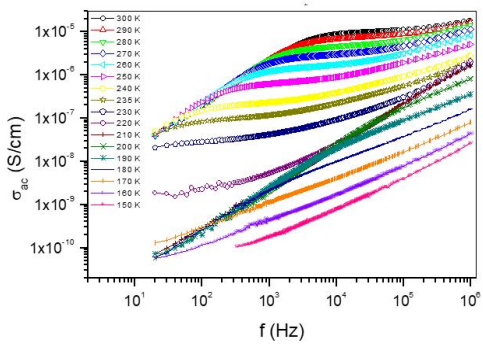

Fig.-6: Behaviour of Dielectric Permittivity in Confined Water

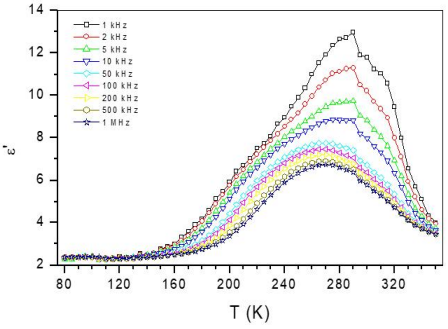

Fig.-7: The Real Permittivity of Water-Loaded MCM vs Frequency and Temperature

Real Permittivity Versus Temperature

Over a range of frequencies, the graph shows how the real part of the permittivity (ε′) of calcined MCM (mesoporous silica material) changes with temperature (T). ε′ stays almost constant at lower temperatures, suggesting that the material's capacity to store electric energy is largely independent of temperature in this range. But the permittivity starts to rise sharply as the temperature rises, especially above a certain point. Compared to higher frequencies like 1 MHz, this increase in ε′ is more noticeable at lower frequencies like 500 Hz. Slower polarization mechanisms, like dipolar or interfacial polarization, may be more active at low frequencies, where they have more time to react to the applied electric field, according to this frequency-dependent behavior. Consequently, the content displays at lower frequencies, like 500 Hz; this increase in ε′ is more noticeable than at higher frequencies, like 1 MHz. Slower polarization processes, like dipolar or interfacial polarization, may be more active at low frequencies, where they have more time

to react to the applied electric field, according to this frequency-dependent behavior. Consequently, at higher temperatures, the material shows a higher permittivity at these frequencies. The presence of water molecules adsorbed within the MCM material's porous structure is probably what causes this polarization to be temperature-sensitive. These water molecules may become more mobile, reoriented, or even partially desorbed as the temperature rises, which would increase their contribution to the total polarization. A temperature-dependent polarization mechanism linked to the behavior of adsorbed species within the mesoporous network is thus highlighted by the observed enhancement in permittivity, especially at lower frequencies.

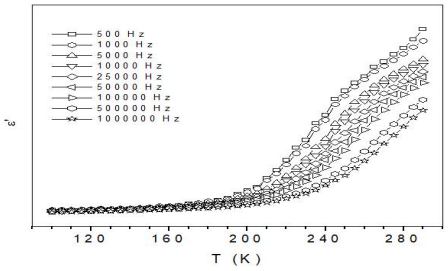

Fig.-8: The Real Permittivity of Water-Loaded MCM vs Frequency and Temperature of 2.7 nm Pore Size

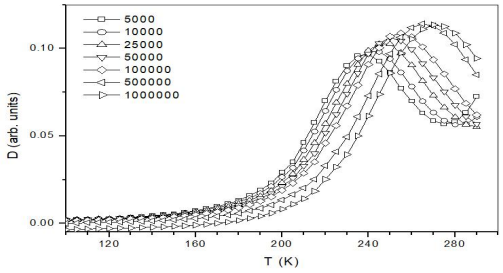

Fig.-9: The Real Permittivity of Water-Loaded MCM Vs Frequency and Temperature of 2.7 Nm Pore Size

Figure-8 shows the Dielectric Loss vs. Temperature in the Second Graph. For various frequencies, the graph displays the dielectric loss (D) as a function of temperature. Figure-9 indicates that the dielectric loss spectrum shows a peak, signifying a relaxation process. As the frequency rises, the peak moves to higher temperatures, a feature of thermally triggered dipolar relaxation. The movement of water molecules trapped inside the MCM pores is probably what caused the observed relaxation.

CONCLUSION

Liquid water exhibits unique properties that distinguish it from most other liquids. Both theoretical and experimental investigations into the dynamic behaviour of liquid water have been ongoing for several decades. Among these studies, the phenomenon of supercooling has attracted significant attention because of its complex nature and fundamental importance in understanding water's anomalous behaviour. MCM-41, with pore diameters of 2.2, 2.5, and 2.7 nm, is used to study how nanoscale confinement affects the dielectric response of water. The study examines the dielectric behaviour of water contained in these materials throughout a temperature range of 80 K to 300 K. Most results demonstrate the crucial role that pore size plays in the relaxation and dielectric response processes. For water contained in 2.7 nm pores, a huge dielectric constant ($\varepsilon' \sim 10^4$) was found, exhibiting characteristics similar to those of known high-dielectric-constant materials. The reorientation of interfacial water molecules is responsible for the Arrhenius behaviour of the low-temperature relaxation (160–220 K) and the non-Arrhenius behaviour of the high-temperature relaxation (230–280 K), which is only seen in pores ≥2.5 nm. The latter suggests that the confinement has an impact on cooperative dynamics. The dynamics of supercooled water in nano-confined settings can be better understood by observing frequency-dependent fluctuations in peak temperatures in both relaxation stages. The work emphasises how important mesoporous structures—like MCM-41 are for facilitating in-depth investigations because of their huge surface areas and consistent pore diameters. With ramifications for material science, nanotechnology, and water-related phenomena in

constrained geometries, these discoveries advance our knowledge of the structural and dynamical characteristics of H_2O in confinement.

ACKNOWELDGEMENTS

This research was supported by the personal resources and academic endowment of the author(s). There was no external financial assistance.

CONFLICT OF INTERESTS

The authors of this article affirm that they have no competing interests in the study, authorship, execution, and publication of this work.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Energy*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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