

# Dielectric studies of some nano-confined liquid thin-films

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## Abstract

The dielectric properties at X band (10.74 GHz) of nano-confined liquid thin-films of methanol, ethanol, isopropyl alcohol and cyclohexane on borosilicate glass substrates are reported here. The pores were observed to have a size distribution in the range of 5–50 nm as observed from SEM studies. The anomalous reduction in the dielectric permittivity is attributed to the increased volume to surface ratio at these dimensions.

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**Keywords:** Dielectric; Confined liquid; Microwave; Nano-liquid film

## 1. Introduction

Although a large literature is available for the dielectric properties of liquids [1–3] and the interactions of the molecules therein [4,5], there are very few studies available on the dielectric properties of confined liquids, and an extremely small fraction of it is dedicated to high frequency measurements. Over the last few years there has been an active interest in the determination of various physical properties of liquids confined to nano pores [6–11]. Most of the properties show anomalous behavior due to the large increase in the volume to surface-area ratio of the nano pores. Such properties are of particular interest in the field of MEMS [12] (micro electro mechanical systems), NEMS [13] (nano electro mechanical systems) and various biological systems. The dielectric properties of liquids confined to nano pores are of importance to device technologies because minute quantities of liquids are adsorbed either physically or chemically onto solid substrates. These liquids can cause a dramatic variation in the energy storage and energy handling capability of the device by the virtue of the altered dielectric permittivity since the capacitance is a direct function of the dielectric permittivity of the material.

It is well established that the molecular dynamics of polar molecules is altered when they are under spatial confinement [8]. The three main reasons for the change in molecular dynamics at

the nano scale are structural effects, surface effects and finite size effects [14]. Structural effects refer to the steric hindrance offered to the molecules by the finite volume of the pores. Surface effects allude to the modified molecular interaction at the boundaries of confinement. Finite size effects are important for glass forming liquids wherein the geometric length scales are shorter than the intrinsic length scales of the molecular dynamics. Distinct dielectric relaxation times have been observed for nano-confined liquids. The fast relaxation time is attributed to the molecules confined to the nano pores and the slow relaxation time to the molecules that form the bulk liquid outside the pores and an additional frustrated layer at the interface of the solid–liquid is also reported [15].

Most of the literature available on the studies of the dielectric relaxation of liquids confined to nano pores in glass is restricted to the study of highly viscous or glass forming liquids such as propylene glycol, *N*-methyl- $\epsilon$ -caprolactan, 2-methyltetrahydrofuran etc confined to controlled porous glasses [16,17,8] with a view to understand the molecular dynamics of such systems, or a study of dielectric dispersion with respect to temperature and pressure [18]. Also a large percentage of the available data is confined to the measurement of low frequency permittivity, up to a few MHz [19]. Since our primary aim is to understand the change in the dielectric properties of liquids confined to pores and their subsequent influence on device performance of MEMS and NEMS at high speeds/frequencies, the present work is restricted to the study of small molecules that are met in MEMS and NEMS fabrication process at microwave X band frequency. At the

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microwave frequencies the orientational polarization has the maximum influence on the dielectric permittivity for small molecules. Further the orientational polarization and its changes are pointers to the nature of bonding that takes place in the system under study since stronger bonds or highly ordered structures will lead to lesser degrees of freedom for the molecular rotation, thus influencing the orientational polarization.

## 2. Materials used

The chemicals chosen for the present study are methanol ( $\text{CH}_3\text{OH}$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), isopropyl alcohol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) and cyclohexane ( $\text{C}_6\text{H}_{12}$ ). These liquids are utilized in the fabrication of MEMS and NEMS. Isopropyl alcohol is used extensively as a drying agent in device fabrication and cyclohexane is a rinsing agent. Methanol and ethanol are not only cleaning and drying agents, but together with isopropyl alcohol, form a homologous series of the first few alcohols. The systematic study of homologous series is advantageous in the understanding of the underlying interactions since it clearly enunciates the effect of the functional group and that of the alkyl chain. Cyclohexane is of further interest since it is a nearly spherical molecule, unlike the linear chain structure of the other compounds. Also it has density, surface tension and viscosity values similar to those of alcohols as seen from Table 2.

All chemicals were of purity >99.8% and were used without further purification. The glass substrates were borosilicate glass microscope slides of thickness 1.187 mm. They were cleaned with soap and distilled water and heated in an oven at 200 °C for 1 h. The plates were then placed in a 2 watt ultrasound sonicator filled with the sample liquid and allowed to sonicate for 15 min at 55 °C so that the pores get completely filled by capillary wetting. After removing from the sonicator, the plates were allowed to cool to room temperature. The thickness of the film thus formed was calculated by measuring the weight of the sample before and after the deposition of the films using a precision electronic balance with an accuracy of  $1 \times 10^{-5}$  g. The weighing was repeated after a period of five days and the films were found to be stable. The dielectric measurements were performed on both occasions and no change in the properties was noticed. The data reported here are those collected just after the preparation of the film.

The average pore size of the glass substrate was determined from the Scanning Electron Micrographs (SEM). The surface of the borosilicate glass was found to have a distribution of pore dimensions varying between 5 and 50 nm, with a predominance of the lower sized pores. The entire substrate surface was found to be uniformly filled by these pores.

## 3. Experimental technique for dielectric measurements

The diameters of the molecules reported in Table 2 are calculated using the CHEMSKETCH software. The complex dielectric permittivity of the glass substrate and the thin liquid films at X band (10.74 GHz) was determined by the cavity perturbation technique.

Cavity perturbation technique is widely used in the measurement of dielectric parameters of materials [20]. Cavity per-

turbation technique has also been used effectively to determine the complex permittivity of liquids [21] for many years.

In the conventional cavity perturbation technique the changes in the resonant frequency and quality factor  $Q$ , when a material is introduced into the cavity give a measure of the complex permittivity of the material [22]. For materials having complex permittivity  $\epsilon' - j\epsilon''$  these changes may be expressed as

$$\frac{f_1 - f_2}{f_2} = (\epsilon' - 1) \frac{\int_{V_s} E_1^2 dV}{\int_{V_c} E_1^2 dV} \quad (1)$$

$$\left[ \frac{1}{Q_2} - \frac{1}{Q_1} \right] = \epsilon'' \frac{\int_{V_s} E_1^2 dV}{\int_{V_c} E_1^2 dV} \quad (2)$$

$$\text{Where } E_1 = E_{10} \sin(\pi x/\alpha) \sin(n\pi z/L) \quad (3)$$

and  $f_1$ ,  $f_2$  are the resonance frequencies without and with specimen respectively.  $Q_1$  and  $Q_2$  are the corresponding quality factor of the cavity and  $V_s$  and  $V_c$  are the sample and cavity volumes respectively.

By substituting Eq. (3) in Eqs. (1) and (2) and solving we will get the equations for dielectric constant and loss as below.

$$\epsilon' = \frac{V_c(f_1 - f_2)}{2V_s f_2} + 1 \quad (4)$$

$$\epsilon'' = \frac{V_c}{4V_s} \left( \frac{1}{Q_2} - \frac{1}{Q_1} \right) \quad (5)$$

The experimental measurements were performed using a  $\text{TE}_{10n}$  rectangular cavity. The rectangular cavity is connected to a Vector Network Analyzer (Model Agilent 8722ES) through a coaxial to wave-guide adapter after the one port calibration. The cavity was excited in  $\text{TE}_{107}$  mode because only at this mode the sample placed centrally is at the maximum electric field position. The block diagram of the experimental setup is shown in Fig. 1.

A glass slide of thickness 1.187 mm and width 5 mm was taken and cleaned properly and placed inside the cavity through

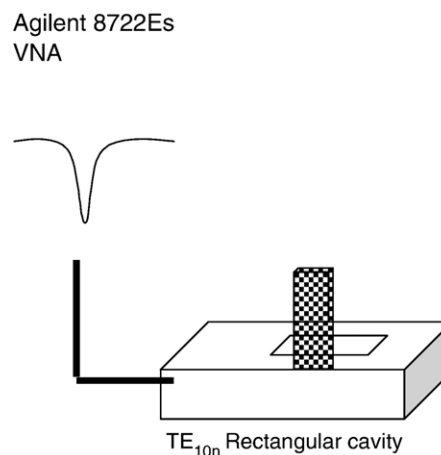


Fig. 1. Block diagram of the experimental setup.

the slot at the center of the cavity. The resonance frequency  $f_1$  and half power width ( $\Delta f$ ) were measured for the selected peaks and  $Q_1$  for the cavity with substrate is calculated ( $Q_1 = f_1 / \Delta f$ ). The glass slide is then coated with a thin layer of respective liquids. This test sample is again inserted into the cavity and the corresponding resonance frequency  $f_2$  and quality factor  $Q_2$  are determined for both the resonances. The experimental results of  $\varepsilon'$  and  $\varepsilon''$  are obtained from the modified Eqs. (4) and (5).

#### 4. Results and discussion

The thickness of the liquid films, the dielectric constant of the glass substrates and the real and imaginary part of the complex permittivity of the liquid films are reported in Table 1. The dielectric permittivity of the thin liquid films is seen to reduce drastically compared to both the static dielectric permittivity and that reported at X band (10.74 GHz) for all the polar samples. The dielectric permittivity of the non-polar sample is seen to show a small increase in value as compared to the static permittivity.

One of the main difficulties encountered while studying the dielectric properties of confined liquids is the fact that the experiments give the entire data of the substrate+liquid system and not that of the individual species. This is much against the general picture in the dielectric study of liquids where the experiment acts as an effective local probe [14]. Hence the data in the present study can only be interpreted as a combined effect of the substrate+liquid system.

The reduction in the dielectric permittivity of the polar samples is attributed to the confinement of the molecules to the pores of the glass substrate hence forming distinct molecular regions. The molecules that are trapped in the pores form one component, the liquid film that forms on the surface of the substrate forms the

Table 2

Some physical properties of the chosen liquids [26]

Liquid	Molecular diameter (Å)	Density (g/cm)	Surface tension (dyn/cm)	Viscosity (cp)
Methanol	3.47	0.791	22.70	0.514
Ethanol	3.72	0.789	22.39	1.074
Isopropyl alcohol	3.93	0.781	22.01	2.038
Cyclohexane	4.30	0.774	24.98	0.894

second component and the interfacial layer the third. As mentioned earlier, as in the case with liquids confined to the pores of a glass substrate/bead etc, the total molecular dynamics of such confined liquids is due to the contribution of all three components.

At the nano-pore level, the surface area predominates over the volume. The liquid molecules are thus exposed to a larger surface area as compared to a bulk sample. In the presence of a large surface area, more molecules undergo bonding with the surface molecules of the substrate. In the present case, since the substrate is a non-passivated glass, a large number of Si–OH bonds exist on the surface. These surface bonds are responsible for the enhanced bonding of the liquid molecule to the surface. This is especially so in the case of polar molecules such as alcohols where there is a preference for the formation of hydrogen bonds. The presence of hydrogen bonds in a system can drastically alter the dielectric properties of the system [5] since there is a change in the orientational polarization thus leading to a change in the net dipole moment of the system. It has been observed from solvation dynamics studies that if the pore size is <1500 nm the liquid molecules confined into such pores have vapor pressure similar to that of a gas and if the pore size is >1500 nm the vapor pressure is similar to that of a liquid. On the other hand, it has been observed that in liquids such as ethylene glycol in a zeolite, five molecules are representative of a single-molecule like behavior and six molecules behave like a liquid [23]. In the present study it is seen that there is a drastic fall in the value of dielectric permittivity for alcohols. This is possible if the molecules in the pores have a gas like behavior, in other words, if the clusters of the alcohol molecules are broken so as to form smaller clusters or independent molecules. The former case of formation of smaller clusters is more likely since the pore sizes are much larger than the molecular diameters. Some of the relevant physical parameters of the molecules chosen for the present study are given in Table 2.

At low frequencies (<10 MHz) the dielectric permittivity of the thin films formed by liquids on porous materials such as butyl rubber [16] is seen to increase with respect to the static permittivity of the host system. In the present study, glass is the host system and no such systematic variation in the value of the permittivity is seen for alcohols but the same is observed for cyclohexane. The increase in permittivity was seen in samples where the adsorbed film thickness was of the order of a few nm where as in the present case the thickness is around a hundred nm, thus leading to a larger interfacial area and the presence of a larger volume of free liquid film layer. The presence of a larger film area leads to the situation where there is a larger number of molecules that form uniform layers thus leading to the formation of a stable film. In such a case the orientational polarization, which is the

Table 1  
Film thickness and permittivity values for the chosen systems

Liquid	Thickness (nm)	$\varepsilon_{\text{static}}$ [26]	$\varepsilon_{\infty}$ [26]	$\varepsilon'$ (glass)	$\varepsilon''$ (glass)	$\varepsilon'$ (glass+liquid film)	$\varepsilon''$ (glass+liquid film)
Methanol	111.3	33.0	1.7657	3.049	0.0227	2.671	0.0336
	120.6			2.958	0.0245	2.765	0.0384
	109.8			2.966	0.0258	2.629	0.0332
	115.3			3.014	0.0248	2.436	0.0348
	112.8			3.032	0.0235	2.484	0.0305
Ethanol	75.0	25.3	1.8526	3.016	0.0245	3.884	0.0572
	74.2			3.119	0.0298	3.794	0.0564
	79.8			3.043	0.0258	3.807	0.0567
	82.5			3.054	0.0279	3.775	0.0496
	68.6			3.044	0.0287	3.436	0.0500
Isopropyl alcohol	139.5	20.187	1.8978	3.025	0.0265	2.897	0.0653
	135.7			3.190	0.0236	2.878	0.0671
	145.9			2.905	0.0217	2.762	0.0681
	120.5			2.930	0.0288	2.884	0.0629
	129.8			3.058	0.0261	3.140	0.0687
Cyclohexane	29.8	2.02	2.0263	3.016	0.0252	2.720	0.0329
	28.4			3.003	0.0278	2.638	0.0307
	22.6			2.986	0.0257	2.767	0.0344
	24.8			3.031	0.0267	2.917	0.0324

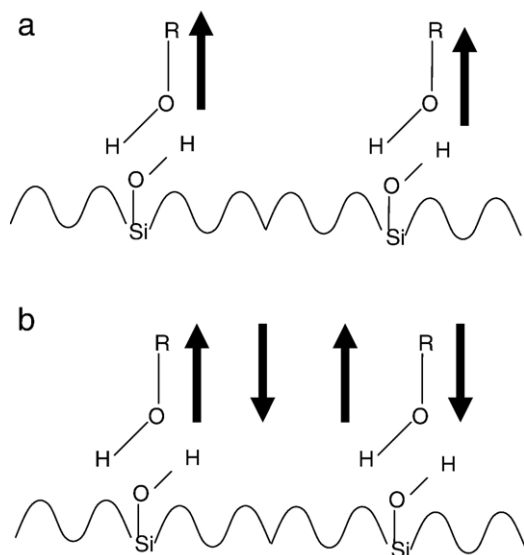


Fig. 2. (a) The proposed interaction of alcohols with the surface of the substrate in the bulk. (b) The proposed interaction of the alcohol molecules with the surface when confined to nano pores. The thick arrow represents the direction of the dipole of the alcohol molecule and R stands for the respective alkyl chain.

direct consequence of the rotation of the dipole, is heavily restricted, leading to a lowering of the dielectric permittivity. This fact is further confirmed in the present case by the low loss ( $\epsilon''$ ) values. The restriction of the orientational polarization can be understood as follows. There must exist a strong bonding between the liquid molecules and also between the liquid molecules and the solid surface in order to enable the formation of a stable liquid film that retains its stability even after five days. Any non-bonded molecule would have evaporated. If there is a strong bonding, then the molecules ought to be aligned such that the liquid film is stable, and hence the free orientation of the molecules in comparison to their liquid phase counterparts must be heavily restricted.

Previous study on the low frequency dielectric properties of acetonitrile confined to glass nano pores has indicated that the pore filling is non-uniform and the adsorbed layer has a dielectric behavior that is different from that of the pore filling [24]. This fact also contributes to the change in the permittivity.

In the case of the thin film of cyclohexane on borosilicate glass, since the liquid is non-polar, the thickness of the film formed on the surface is very small compared to that of the polar liquids. The dielectric permittivity of the substrate+liquid is intermediate to that of both substances, with a value closer to that of glass. Also, the finite loss factor is a contribution from the substrate. Hence it is seen that capacitance of the glass+cyclohexane is altered by the liquid thin-film, with the substrate having a predominating effect. It is the non-polar nature of cyclohexane that is important here and not the physical properties such as viscosity, surface tension and density. This observation is of value since for film thickness less than a few monolayers, the physical properties play a crucial role in the overall physical properties.

The schematic representations of the suggested surface-molecule interactions are given in Fig. 2. These are based on the suggested interactions of acetone, DMSO and DMF with porous

glass surface based on Raman scattering experiments by Czeslik et al. [25]. Here the interactions in the adsorbed liquid film are similar to that in the bulk. In the case of confinement, since the molecules are much closer to one another, a local ordering takes place leading to an anti-parallel orientation of the dipoles of the alcohol molecules. The actual nature of ordering of the intermediate layer is difficult to envisage since the steric hindrance offered by the uneven boundaries to the clusters of molecules has to be taken into account.

## 5. Conclusion

The dielectric properties at microwave X band (10.74 GHz) of nano-confined liquid thin-films of methanol, ethanol, isopropyl alcohol and cyclohexane are reported. To the best of our knowledge, this is the first time that these data are reported. A drastic reduction in the real and loss part of the complex permittivity of the systems is seen for the alcohol thin films when compared to the permittivity values of pure alcohols. A slight increase in the permittivity of the cyclohexane thin-film when compared to that of pure cyclohexane is seen. Further studies on the properties of these nano-confined liquid films at various frequencies will enable the determination of the resonance frequency corresponding to the dipolar reorientation. The chemicals chosen for the present study are important for the fabrication of present day devices such as MEMS and NEMS. A reduction in the dielectric permittivity directly translates to a reduction in the energy storage capacity of the device. Also depending on the effective capacitance (series or parallel), the minute amounts of liquid adsorbed either physically or chemically onto the pores of the substrate can considerably change the electrical properties of the device. Hence the present findings are important for the understanding of the electrical properties of devices such as MEMS and NEMS.

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