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Dielectric studies of some nano-confined liquid thin-films

V. Madhurima, K. Sudheendran, K.C. James Raju *

School of Physics, University of Hyderabad, Hyderabad 500046, India

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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.

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-ε-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

* Corresponding author.
E-mail address: kcjrsp@uohyd.ernet.in (K.C. James Raju).

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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 (CH_3OH), ethanol (CH_3CH_2OH), isopropyl alcohol ($CH_3CH_2CH_2OH$) and cyclohexane (C_6H_{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 1×10^{-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 perturbation 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 $\varepsilon'-j\varepsilon''$ these changes may be expressed as

$$\frac{f_1-f_2}{f_2}=(\varepsilon'-1)\frac{\int_{V_s}E_1^2\mathrm{d}V}{\int_{V_c}E_1^2\mathrm{d}V} \tag{1}$$

$$\left[\frac{1}{Q_2}-\frac{1}{Q_1}\right]=\varepsilon''\frac{\int_{V_s}E_1^2\mathrm{d}V}{\int_{V_c}E_1^2\mathrm{d}V} \tag{2}$$

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

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.

$$\varepsilon'=\frac{V_c(f_1-f_2)}{2V_sf_2}+1 \tag{4}$$

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

The experimental measurements were performed using a 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 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

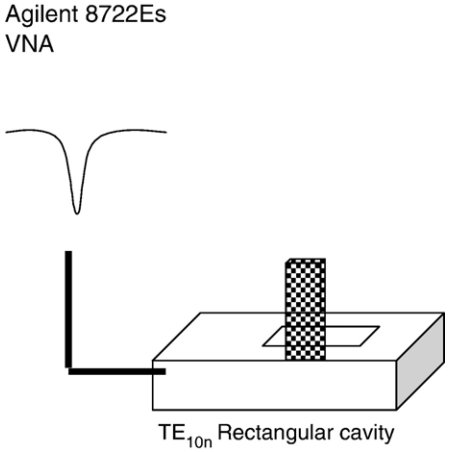

Fig. 1. Block diagram of the experimental setup.