



Research paper

Correlation between salt-induced change in water structure and lipid structure of multi-lamellar vesicles observed by terahertz time-domain spectroscopy



Da-Hye Choi*, Heyjin Son, Jin-Young Jeong, Gun-Sik Park

Center for THz-Bio Application Systems, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Republic of Korea

ARTICLE INFO

Article history:

Received 27 May 2016

In final form 12 July 2016

Available online 14 July 2016

Keywords:

Hydrogen bond network

NaCl

Small-angle X-ray scattering

Terahertz spectroscopy

Water molecules

ABSTRACT

Salt-induced change in the structure of water molecules inside multi-lamellar vesicles is experimentally studied with terahertz time-domain spectroscopy. The complex dielectric constant of 1, 2-ditetradecanoyl-sn-glycero-3-phosphocholine model membranes dispersed in NaCl solution with different salt concentrations are measured. Structure of water molecules in the solution is characterized from the measured dielectric constant using Debye relaxation model. Combined with small-angle X-ray scattering observation, it is found that salt-induced change of water structure, especially fast water fraction, show strong correlation with the increase in nanometer-scale multi-lamellar repeat space. This suggests that water could be critical in nanometer-scale membrane-membrane communications.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In living organisms, critical biological processes such as membrane fusion and secretion take place in salt solutions containing various ions. The influence of the ions on structural change of membranes, which is an inevitable step during the processes [1], has been extensively studied using model membranes. For example, ions can trigger aggregation and fusion [2,3] of vesicles and phase separation of lipid bilayers [4,5]. The striking effect of ions to membrane structure has highlighted that lipid-ion interactions are important in biological processes.

Another excellent example showing the salt-induced structural change of membranes is swelling of multi-lamellar vesicles (MLV) in salt solutions [6]. The addition of salts to MLV modifies the force balance maintaining the structure, and the modification can be sensitively observed in the change of multi-lamellar repeat distance D with small-angle X-ray scattering (SAXS). Petrache et al. [6] quantitatively explained that swelling is induced by weakening of van der Waals attraction between lipid layers by measuring D depending on salt concentrations. In this explanation, effect of water molecules inter-spacing lipid layers was considered to have minor effect due to much shorter range of hydration ($1\text{--}2\text{ \AA}$ [7]) than typical D ($50\text{--}70\text{ \AA}$ [8]).

While another researchers [9,10] agree that van der Waals interactions play a role, some report suggested [10] that the

increase in the hydration force with the addition of salt has also to be taken into account. More importantly, recent study [11] reported that salt-specific lamellar swelling cannot be explained without considering water effect. Also, there are evidences showing that different hydration state is found in the phase transition of the lipids [12,13], which imply the correlation between water and membrane–membrane interactions. However, there is no clear evidence correlating the hydration state of lipids and membrane-membrane interaction in nanometer-scale space.

Terahertz (THz) spectroscopy has been proved to be a powerful technique for characterizing nanometer-scale long-range hydration water around various biomolecules [14–16] including lipid bilayers [17]. Also, recent study investigated changes of the nm-sized hydration layer during the course of hydrophobic collapse using time-resolved THz spectroscopy [18]. In the present study, we experimentally investigate the salt-induced change in water structure inside MLV with THz spectroscopy. Combined with SAXS observation, we show that salt-induced change of water structure, especially fast water fraction, is correlated with multi-lamellar spacing increase in nanometer scale.

2. Materials and methods

DMPC lipids used in this study were purchased from Avanti Polar Lipids, Inc. (Alabaster, AL) in powder form and were used without further purification. The NaCl solution was purchased from Sigma-Aldrich. The powder samples were fully hydrated with pure water or the NaCl solutions to form 117 mM lipid

* Corresponding author.

E-mail address: dahyechoi7@gmail.com (D.-H. Choi).

concentration to avoid unusual properties from arising in the partially hydrated condition [19]. The solutions were vigorously vortexed to form MLV.

Because phase behavior of lipid solution is critical to water dynamics [12], we investigated phase behavior of lipid solutions with differential scanning calorimeter (Discovery DSC, TA Instruments). The system is composed of a measurement cell with a refrigerated cooling system and a computer-based controller. Reference and sample pans were placed within the cell by an auto sampler. The phase transition temperature of the lipid solutions were measured between temperatures from 10 to 40 °C at a heating rate of 1 °C/min.

Complex dielectric constant of fully hydrated lipids were measured using a THz TDS system (TAS7500SP, ADVANTEST Co.) with an attenuated total reflection (ATR) module in the frequency range from 0.3 to 1.2 THz. In the THz TDS system, temporal form of THz wave is recorded with and without a sample. The temporal THz waveform with the sample experience both amplitude decrease and time delay compared to the waveform without the sample. After Fourier transformation of the THz waveform, we can simultaneously obtain both the reflectance $R(\omega)$ and phase shift $\varphi(\omega)$. Therefore, the complex dielectric constant of the sample can be calculated directly with the obtained parameters. The detailed calculation to determine the complex dielectric constant of the sample is well explained in the literature [20]. Temperature was attached to ATR prism to control and maintain the sample temperature within ± 0.1 °C.

The conductivity σ of lipid solutions with ions was determined by a conductivity meter (S230 SevenCompact™ conductivity, Mettler Toledo Inc.).

In order to check the repeat distance D of MLV used in the experiment, SAXS experiment was performed using the 4C SAXS II beamline at Pohang Accelerator Laboratory (PAL). The X-ray energy is 18.360 keV, pixel size 0.0796 mm, and sample to detector distance is 2 m. The repeat distance D was obtained from the peak position q ($=2\pi/D$).

3. Results and discussions

We previously reported that phase of DMPC is critical to water dynamics [12]. First, we check the ion-induced change in phase-transition temperature of the lipid solutions with differential scanning calorimeter (DSC). The shift is from 11.8 to 21.7 °C and from 23.0 to 25.5 °C for the pre- and main phase transition, respectively (Fig. 1). We fixed the temperature to 28 °C, at which all of the samples are in fluid phases for all measurements.

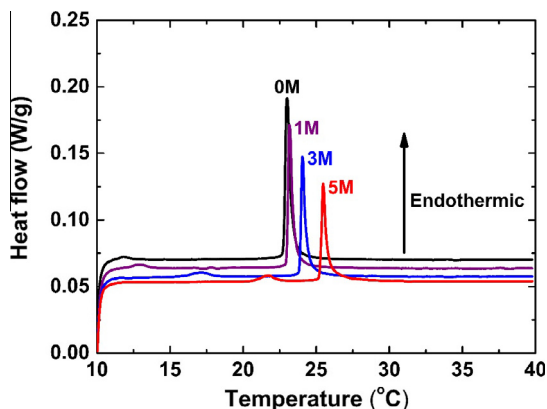


Fig. 1. DSC curves of lipids dispersed in NaCl solutions with different concentrations.

Fig. 2 presents the complex dielectric constant of lipid solutions with different NaCl concentrations. The real part of the dielectric constant increases monotonously with NaCl concentration for all frequency in the study, whereas the imaginary part of the dielectric constant shows a rather weak dependence on the NaCl concentration at low frequencies, and displays a less significant increase with NaCl concentration at high frequencies. The observed behavior is similar to the frequency-dependent dielectric response of pure NaCl solutions in the microwave region by Buchner et al. [21] and in the terahertz region by Jepsen et al. [22]. In the frequency region studied here (0.3–1.2 THz), the dielectric relaxation of water molecules in pure liquid water and ionic solutions is well described with the Debye model [22–24]. Because imaginary part of the dielectric constant of DMPC film is almost zero and dispersionless in the frequency region investigated in this study [12,17], we assume that the frequency dependent dielectric response of the lipid solutions stems mainly from the dielectric response of the water molecules with an additional contribution of the ionic conductivity. In the terahertz region, there are several active mode of water molecules including dielectric relaxation mode which is the dominating one [25]. We restrict our frequency range up to 1.2 THz to avoid additional contributions from bending mode (~ 1.8 THz), hydrogen bond stretching mode (~ 5.4 THz) of water molecules and ionic cage mode (~ 3.6 THz and ~ 5.4 THz) [26] to the dielectric response. We fitted the experiment data using a model containing two Debye terms and ionic conductivity [22] as follows ($n = 2$ in Eq. (1))

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_i^n \frac{S_i}{1 - i\omega\tau_i} + i \frac{\sigma}{\omega\varepsilon_0}, \quad (1)$$

where τ_i is Debye relaxation time, S_i represents the dielectric relaxation strength with the time constant τ_i , ε_{∞} is dielectric constant at the high-frequency limit, σ is the ionic conductivity, and ε_0 is the permittivity of free space. In our fits, the parameters in the model, ε_{∞} , τ_i , and S_i were varied simultaneously but fixing the independently measured conductivity σ . The solid lines in Fig. 2 are fit to the experiment results.

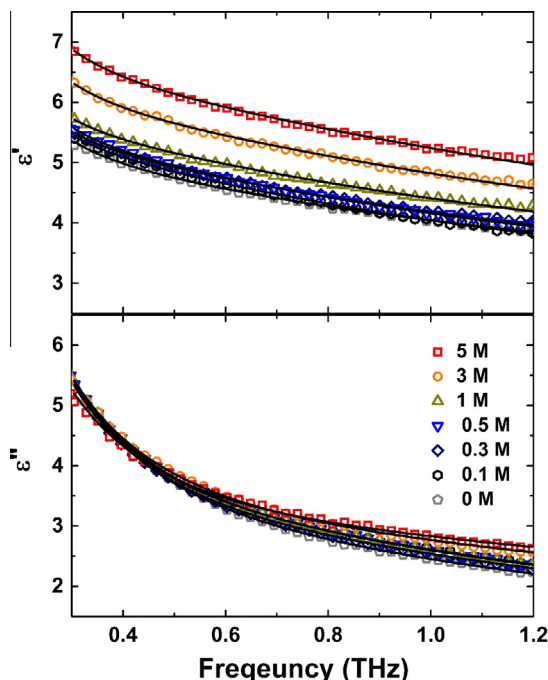


Fig. 2. Dielectric constant of lipids dispersed in solutions at different salinities. Black solid lines are Debye fit to the data.

Download English Version:

<https://daneshyari.com/en/article/5378778>

Download Persian Version:

<https://daneshyari.com/article/5378778>

[Daneshyari.com](https://daneshyari.com)