



Time domain dielectric relaxation studies of amphiphilics in solution state



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ABSTRACT

In liquid state, the amphiphilic molecules of acids and alcohols form a two dimensional array of an air–water interface. The structure of amphiphilics and the affinity of polar groups towards the environmental dipoles determines the stability of the two dimensional array. The amphiphilics substances are related to the formation of monolayers and multilayers in various substrates. The majority of the carboxylic acids with the low alkyl group are said to exist in a dimeric form of an open or closed structure. The structure of the film and the reorientation of hydrophobic tails can be modified by adjusting the surface pressure. Many experimental methods are available to characterize the degree of orientation. A simple, rapid and nondestructive measuring technique, such as dielectric spectroscopy provides information about the dielectric response of materials to electromagnetic fields. The amphiphilic acids of interest with useful optical, electrical and biological properties are characterized by manipulating the head group interactions of the materials. The dielectric polarization studies of the orientation ordering are important in the context of co-operative reorientation of the head group structure. We report here the results of our measurement of the complex dielectric constants ϵ' and ϵ'' over a frequency range of 10 MHz to 30 GHz using the time domain reflectometry (TDR) technique of stearic acid in benzene at various temperatures of 30 °C, 25 °C, 20 °C, and 15 °C. The dielectric relaxation time (τ_0) for carboxylic acids for this temperatures are not found to be reported so far. The average relaxation time (τ_0) shows double for the normal acids. The long chain amphiphilic acids may have the same possibility of bending and twisting orientation. The result interprets in terms of dynamic response of the polarization field of the medium which is due to the frictional motion of the long chain amphiphilics, which adds to stokes viscosity friction.

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1. Introduction

Amphiphilics contains both hydrophilic and hydrophobic parts, which are linked on the basis of covalent bonds [1]. Amphiphilics can self-assemble in water to form various well defined molecular assemblies such as micelles and vesicles [2]. The structure and properties of the assemblies are closely connected to the architecture of amphiphilics [3]. The dielectric relaxation spectroscopic studies of alcohols, solubilized by various long chain amphiphilics in aqueous solution, were studied by Ganesh et al. [4–6].

The concept of amphiphilics has been extended to polymers, fatty acids (or) carboxylic acids. Generally a polymeric (or) carboxylic amphiphilic is constructed by linking a hydrophilic and a hydrophobic segment through a covalent bond. Compared with low molecular weight amphiphilics, carboxylic amphiphilics are endowed with structural diversity and stability. The self-assemblies fabricated using polymeric amphiphilics have a larger capacity for guest molecules and better thermal sustainability. The assemblies from low molecular

weight amphiphilics are comparatively dynamic, due to the balance between the aggregated molecules and the dissociated non-aggregated molecules in the bulk solution. In the aggregates from carboxylic amphiphilics, however the stronger interactions as well as the end arrangement between the chains prevent quick molecular exchange. Moreover, the longer molecular chains also provide the aggregates with a larger capacity for guest molecules. The unique property of the fatty acids has led to applications in the self-assembled Monolayer (SAM), drug delivers, Langmuir films and templated synthesis of nanomaterials.

Fatty acids are abundantly available in nature as a main constituent of complex biological substances such as lipids, fatty oils, phospholipids, glycolipids and sphingolipids. It is believed that the physical properties (or) phase behaviour of the macroscopic lipid assemblies are responsible for their biological function in living bodies. The saturated fatty acids provide a flexible property to the molecular assemblies, which are essential for the function of various membrane studies. Physical properties of materials, including dielectric behaviour are governed by the molecular interaction, especially in the case of a mixture system. The balance of interaction between the same molecule and between different molecules is responsible for the phase behaviour.

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Dielectric studies have been carried out extensively to understand intermolecular interactions and dynamics of the liquid mixtures [7–11] using time domain reflectometry. The dielectric measurements have been performed on hydrogen bonded liquids and fatty acids. In 1913 Debye derived an equation and applied it to the dielectric relaxation of an assembly of polar molecules, large molecules and colloidal suspensions, each of which is conceived of as a rigid body rotating about a fixed axis. The only interaction in the static theory is due to the external applied field with each dipole being imagined as a rotating Brownian particle. This is immediately an approximation, as Einstein's theory strictly applies to a very long chain of molecules such as polymers, fatty acids, biological substances and also colloidal substances. The dielectric properties of stearic acid multilayers (SAM) have received a considerable amount of attention over the years, since they provide a useful form of dielectric structure in which the thickness can be varied in multiples of a monolayer, corresponding to the length of a molecules which is in the order of nanometers [12].

The equation originally used by Debye is applicable to the three coordinates

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial f}{\partial x} + \frac{f \partial v}{\xi \partial x} \right) \quad (1)$$

where x is replaced by the azimuthal angle ϕ , and the body being rotated about the 'Z' axis. Then $E_m e^{i\omega t}$ is the applied field along the 'Z' axis so that

$$V(\phi) = -\mu E_m e^{i\omega t} \cos(\phi). \quad (2)$$

Eq. (2) represents the dipole vector on a sphere of constant radius

$$N\mu(\cos\phi) = \frac{E\alpha \tan^{-1} \omega\tau_D}{\sqrt{1 + \omega^2\tau_D^2}} \quad (3)$$

so that the mean dipole moment lags behind the applied field by an angle

$$\tan^{-1} \omega\tau_D \quad (4)$$

and the amplitude is reduced by the frequency dependent

$$1/\sqrt{1 + \omega^2\tau_D^2} \Rightarrow \omega = 1/\tau_D$$

where $\tau_D = \xi/2kT$ is called the Debye relaxation time and η is calculated from the Stoke's law for the viscous torque on a rotating body. $\xi = 8\pi\eta a^3$, where η is the viscosity and 'a' is the radius of the spherical Brownian particle. Typical values of ' η ' and 'a' yield a relaxation time τ of the order of 10^{-12} to 10^{-10} s in the microwave region.

Dielectric spectroscopy associating liquids offer valuable importance in interpreting the bonding characteristics and H-bond interactions in the complex molecular systems. Time domain reflectometry (TDR) is a very useful technique to study the dielectric relaxation parameter of liquids. This technique covers a broadband of frequencies in a single measurement. The low frequency measurements of a conductive system are strongly limited due to electrode polarization. All of the above methods lead to the fact that information on dielectric spectrum over a wide frequency range in a one step pulse (time window) can be used to determine various relaxation parameters. The successful development of the time domain spectroscopy (TDS) method and [13–19] broad band dielectric spectroscopy (BDS) has radically changed the attitude towards DS making it an effective tool for the investigation of solids and liquids on the macroscopic, microscopic and mesoscopic levels. In our present work, the detailed dielectric relaxation studies of stearic acid in benzene solutions at different concentrations and temperatures have been carried out using a time domain reflectometry technique from 10 MHz to 30 GHz. The resulting dielectric parameters such as static dielectric

constant, dielectric constant at infinite frequencies, relaxation time, relative permittivity, viscosity and density of each concentration of stearic acid solutions have been evaluated.

2. Experimental

2.1. Materials

Stearic acid (octadecanoic acid), obtained from Sigma Aldrich, had a purity of about 99% and benzene was obtained from Merck India Pvt. Ltd., Benzene was used as a solvent without further purification. The values of ϵ_0 , ϵ' and ϵ'' for various concentrations of the amphiphilics in benzene at 30 °C, 25 °C, 20 °C, and 15 °C are obtained. The solutions were prepared very carefully and maintained at a desired temperature (10–15 min) before taking the measurements. The mixtures were prepared by weighing appropriate amounts of the constituents into a suitable flask. In order to avoid the uptake of moisture from the air (or) evaporation of a non-volatile solvent tightly packed flasks are used. The dielectric permittivity ϵ' , dielectric loss ϵ'' , static dielectric constant ϵ_0 , relaxation time (τ) and dielectric constant at infinite frequency (ϵ_∞) were measured using time domain reflectometry (TDR) in the frequency range 10 MHz to 30 GHz. The basic TDR setup consists of broad band sampling oscilloscope, TDR model and coaxial transmission line. A Tektronix digital serial analyzer DSA8200 with sampling module 80E08 has been used, and this module provides an accurate oscilloscope measurement with a selectable band width of 10 MHz to 30 GHz. A 200 mv step pulse with 18 ps incident pulse and 20 ps reflected pulse time and 200 kHz repetition rate passes through coaxial 50 Ω impedance lines. The coaxial semi-rigid copper cable E286M17 [Huber Suhner Electronics Pvt., Ltd.,] with that end was used. The dimensions of the used cable are: inner diameter of the outer conductor 2.2 mm, outer diameter of central conductor 0.51 mm and the diameter of the dielectric 1.66 mm respectively. All the measurements were carried out in open load conditions. Sampling oscilloscope monitors change in step pulse after reflection from the end of the line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 2 ns and digitized in 2000 points. The temperature of the dielectric cell can be controlled through a refrigerating cooling system within the accuracy of ± 0.5 °C. The 50 Ω impedance coaxial cable was kept inside the thermo system and a sample was placed inside the chamber for 1–2 min for attaining constant temperature. The temperature can be increased using an external heating device. The solvent benzene is highly volatile and hence the solution was prepared just before taking measurements. After placing the sample inside the thermochamber, 30–40 s is sufficient to get incident and reflected pulse from the sample and the data to be store in the oscilloscope. Before taking measurements of the sample, the instrument should be calibrated for known polar and nonpolar liquids and the corresponding signals are stored in the system. This process was repeated for a long duration and the base line was fixed for each solvent and for mixed solvents. The deviation from the baseline was observed and it showed the error. Before taking measurements, the errors obtained from the device should be very minimum. The signal was obtained through the oscilloscope and using various programmes with an iteration process the error can be eliminated.

An Ostwald viscometer is a commonly used viscometer, which consists of a U-shaped glass tube held vertically for taking measurements. It is also known as a glass capillary viscometer. The time taken for a liquid to flow between the two marks was noted. The Ostwald viscometer is a function both of dynamic viscosity and density. The relationship between dynamic viscosity and density is called the kinematic viscosity and is defined as

Kinematic viscosity = Dynamic viscosity/density.

It measures the kinematic viscosity of the solution. However, if the fluid is Newtonian, the dynamic viscosity can be determined from the

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