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Ultrasonic Velocity And Absorption Measurements In Lyotropic Liquid Crystal Systems

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ABSTRACT

We have measured ultrasonic absorption and velocity in aqueous solution of NaTC(bile salt) in water as a function of temperature and frequency. Ultrasonic absorption measurements have been done in frequency range 5 to 35MHz using pulse-echo technique. Ultrasonic velocity measurements were performed at fixed frequency 2MHz using interferometric technique. Relaxation frequencies have been evaluated using experimental data of absorption at different temperatures. The lyotropic liquid crystalline phase due to micelle formation took place at $\approx 35^0$C at critical concentration 58.4 gm/1000ml of NaTC in water.

KEYWORDS

Ultrasonic measurements;
Micelle formation;
Lyotropic liquid crystal;
Relaxation frequency.

INTRODUCTION

Ultrasonic absorption and velocity studies have been made in variety of the solids[1,2], liquids[3,4], glasses[5,6] and liquid crystals[7,8] in a wide range of temperature, frequency etc. using different theories and techniques. There are several books and review articles [9-12], which give different studies of chosen lyotropic liquid crystal systems(NaTC+water). The peculiar beha viour of compressibility and electric conductance have been reported at the concentration 58.4gm NaTC per 1000ml water at 35^0C[9]. Bile salts are very interesting materials, which are used for formulation of pharmaceuticals. Bile salts used as surfactant, those are metabolic by-products. The measurements are useful not only justification of liquid crystalline state, but also in medical and biological applications.

EXPERIMENTAL

H_2O and NaTC were taken as sample materials. NaTC used in present work was supplied by Loba Chemie India Ltd. of stated purity 97% and 65% bile acid content. Used H_2O was having 99% purity. No further purification has been done in NaTC and water. Sample was prepared with 58.4gm of NaTC in 1000 ml of water by heating up to 60^0C for several hours, then cooled up to room temperature. Prepared sample was of light yellow colour.

For ultrasonic characterization we have measured the ultrasonic velocity in the temperature range 30^0C to 40^0C at critical concentration 58.4gms of NaTC in

1000ml of water using ultrasonic interferometric technique at fixed frequency 2MHz. The temperature variation is accurate to $\pm0.5^0$C and velocity $\pm0.1\%$. Ultrasonic absorption measurements of the sample have been done at frequencies 5MHz, 10MHz, 15MHz, 25MHz and 35MHz between temperature range 30^0C to 40^0C using pulse-echo technique. Water from a thermostat is circulated around the sample to keep the temperature constant. The accuracy in the absorption measurement is $\pm5\%$. Several known values of standard liquids were checked, including water so as to have satisfaction in absorption and velocity measurements. The observations were repeated several times.

RESULTS AND DISCUSSION

The measured ultrasonic velocity in the present sample using interferometric technique is shown in figure1. The ultrasonic velocity in aqueous solution of NaTC at critical concentration (Figure1) increases with temperature and has minima at 35^0C. The velocity (V) is well related to adiabatic compressibility(E) as: $V=(1/E\rho)^{1/2}$; where ρ is density. A rapid increase was found in temperature variation of adiabatic compressibility in present sample at 35^0C[9]. Thus velocity minima seem to be justify by the reciprocal relation between velocity and compressibility. The velocity in water increases with temperature, reaches a broad maximum at 74^0C and decreases thereafter[13]. Besides exception in water, the velocity in liquids generally decreases with temperature. The present anomalous behaviour of ultrasonic velocity can be qualitatively explained in terms of the molecular association of water with NaTC. The velocity minima at 35^0C may be ascribed due to collapse of hydrogen networks or to a significant reduction of hydrophobic interaction.

The temperature at which $\partial k/\partial T$ is maximum/minimum and $\partial^2 k/\partial T^2=0$; k: electrical conductance, is called as transition temperature. There have been found an anomalous minima in the temperature variation of k and thermal stability for the present mixture at 35^0C[9] . This shows a transition from liquid to liquid crystalline phase. A velocity minimum in binary solution with temperature qualitatively explains the formation of micelle at particular concentration and temperature[7].

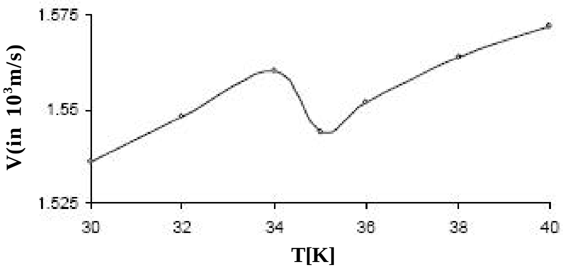

Figure 1 : Ultrasonic velocity vs temperature

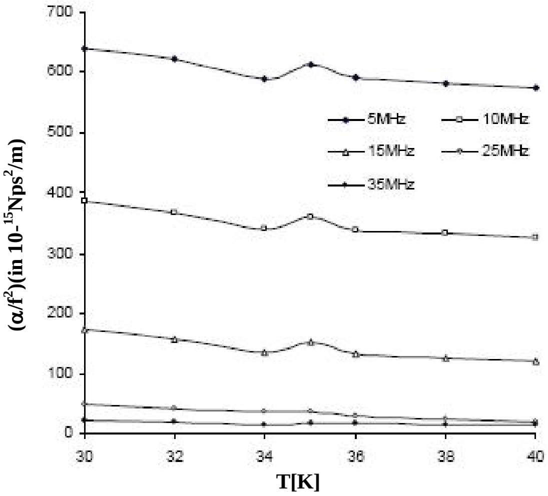

Figure 2 : (α/f^2) vs temperature

The ultrasonic velocity in water at temperatures 20^0C, 30^0C and 40^0C are 1.482×10^3m/s, 1.509×10^3 m/s and 1.529×10^3m/s respectively[14,15]. The present velocities are larger than these values. In anisotropic/crystalline solids, the velocities are larger in comparison to pure liquids. Thus we can say that larger velocities in the sample may be due to its anisotropic nature or crystalline phase. Hence the present study of ultrasonic velocity justifies that aqueous solution of NaTC undergoes liquid to liquid crystalline phase at critical concentration 58.4gm/1000ml and at critical temperature 35^0C due micelle formation.

The measured ultrasonic absorption in present sample is shown in figures 2-3. The temperature variation of α/f^2 has maxima for each frequency at 35^0C. The ultrasonic absorption (α/f^2) is proportional to η/v^3(η: viscosity) for solid/liquids[15]. The variation of α/f^2 with temperature is opposite in nature with respect to temperature variation of ultrasonic velocity. Hence present investigation justifies the relation$(\alpha/f^2)\propto V^{-3}$ and proves the transition in phase of solution. The ultrasonic absorption α in water at 20^0C was found $25\times10^{-}$

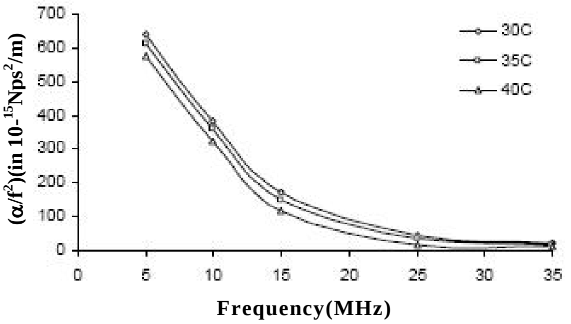

Figure 3 : (α/f^2) vs frequency

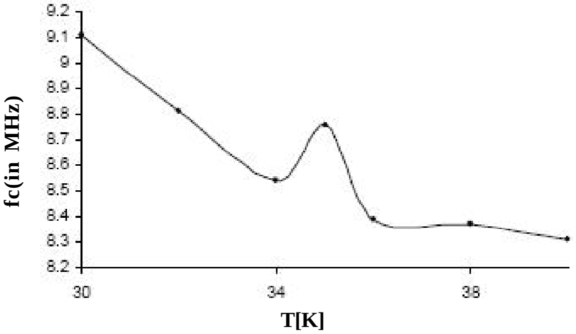

Figure 4 : Relaxation frequency vs temperature

^{3}Np/m, which is equivalent to 10^{-15}Nps^2/m at 5MHz. The present α/f^2 is larger than pure water value as reported in literature[15]. The large value of α/f^2 is due to large volume viscosity caused by mixing of bile salt (NaTC). The viscous mechanism is relaxational in nature and has a volume relaxational frequency[15].

At higher frequencies it appears that the absorption coefficient should increase, assuming that viscosity remains constant while the frequency allowed to increase. This prediction is approximately true over only a limited frequency range for which the effective value of viscosity coefficient is same as the value at low frequencies, that is, under static conditions. As the frequency increases, the effective viscosity decreases monotonically towards zero[15]. Thus α/f^2 decreases with frequency, where viscosity is responsible for absorption. Such characteristic of α/f^2 vs. frequency is found in present investigation (Figure 3). This proves that the viscosity of the sample is predominant factor for ultrasonic absorption. Hence the frequency dependent absorption graph (Figure 3) indicates that the process of transition from liquid to liquid crystalline phase is relaxational in nature, so the solution must have a relaxational frequency at each temperature. In relaxational process, the α/f^2 follows the following relation[15,16].

$$\frac{\alpha}{f^2} = \frac{A}{1+\left(\frac{f}{f_c}\right)^2} + B \qquad (1)$$

where : α: ultrasonic absorption, f: frequency, f_c: relaxational frequency, A: relaxational amplitude and B: constant absorption at higher frequency.

The relaxation frequency for the sample at each temperature has been shown in figure 4. The relaxation frequency decreases with temperature and have characteristic maxima at 35^{0}C, which is an indication of the phase transition caused by the micelle formation.

According to Giglio and co-worker[17-19], long rod like aggregates based on a helical arrangement of bile salt (NaTC) may form in solution causing anisotropic structure when concentration of micellar surfactant exceeds a certain value at certain temperature. The phenomenon is supported by maximum ultrasonic absorption at 35^{0}C(Figure 2).

A microscopic interaction of NaTC molecules with water molecules appears to be critical parameter to control the final ultrasonic absorption. The effective absorption in the sample can be expressed as:

$$\alpha = \alpha_b + \alpha_w + \alpha_{bw} \qquad (3)$$

where α_b and α_w are contribution of BS (NaTC) and water in absorption, α_{bw} describes the change in the final α-value owing to a macroscopic interaction. The parameter α_{bw} includes the effect of the modified structure (lyotropic liquid crystalline nature) of the sample which appears at $\approx$35^{0}C at critical concentration.

On the basis of above discussion the ultrasonic properties of the bile salt(NaTC) with water are very important to detect the lyotropic liquid crystalline phase at critical conditions. Behaviour of ultrasonic absorption and velocity at different conditions with other experimental findings reveals the qualitative information about the liquid crystalline phase appearing in the binary mixture.

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