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Ultrasonic Studies Of CTAB/Decanol/Water Systems

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ABSTRACT

The ultrasonic velocity and the attenuation in the n-cetyl-N, N, N-trimethylammonium bromide(CTAB)+decanol+water lyotropic systems have been measured at different physical conditions like temperature, frequency of the wave and concentration of the components in the solution. The critical temperature and the critical concentration of the component were determined 35°C and 0.5 wt% of CTAB in the solution respectively for the formation of liquid crystalline phase. The characteristics and peculiarities of specific textures, which were spontaneously formed, have been discussed correlating with the other studies.

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KEYWORDS

Lyotropic liquid crystal;
CTAB;
Ultrasonic measurements;
Micelle formation.

INTRODUCTION

Liquid crystals having anisotropy of physical properties display a large number of mesophases. Liquid crystalline mesophases were characterized by different structures and different spatial symmetries therefore display a great variety of textures. These possess different morphological, optical and structural peculiarities^[1-11].

Extensive studies on ultrasonic absorption and dispersion in solids^[12-15], liquids^[16-19], glasses^[20-21], nematic liquid crystals^[22-25], smectic-A liquid crystals^[26-28], cholesteric liquid crystals^[29-33] and lyotropic liquid crystals^[34-41] are reported in the literature. In most of the cases, the phenomena of ultrasonic attenuation were well explained. Different investigators have tried with different theories and techniques to explain ultrasonic behaviour in binary

lyotropic liquid crystals, but in literature few studies have been found to explain the ultrasonic properties of ternary lyotropic liquid crystal systems^[38]. In the knowledge of authors, no ultrasonic studies of ternary lyotropic liquid crystal systems(CTAB+Decanol+water) was found in literature.

The liquid crystals can be classified in to two main categories, thermotropic and lyotropic liquid crystals. Thermotropic transitions occur in most liquids and they are defined by fact, that the transitions to the liquid crystal are induced thermally, while lyotropic liquid crystal transition occur with influence of solvent, not only by the change in temperature.

In the present investigation, we have studied the liquid crystalline behaviour of n-cetyl-N, N, N-trimethylammonium bromide (CTAB)+decanol+water system.

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Ultrasonic absorption measurements have been made as a function of concentration, temperature and frequency. The ultrasonic velocities have also been measured at different concentration and temperature at frequency 2MHz. The significant features of the observation are discussed.

EXPERIMENTAL

The CTAB, used in the present investigation were supplied by Loba Chemmie India Ltd and has stated purity 99%. Decanol, used as aliphatic alcohol was supplied by Johnson Matthey company and has stated purity 99%. The water used as main solvent, was distilled and deionized twice and was 99.9% pure. The 100ml of solvent has 4% decanol and 96% water respectively.

The velocity measurements have been made by a standard variable path interferometer technique at 2MHz. The temperature variation was accurate to $\pm 0.5^\circ\text{C}$ and velocity to $\pm 0.1\%$. For the ultrasonic characterization, we have measured the ultrasonic velocity in the temperature range 25°C to 45°C at the concentrations 0.1wt% to 1.25wt% of CTAB in the solution. The concentration dependent ultrasonic velocities at temperature 25°C are shown in figure 1. Variation of the ultrasonic velocity with temperature at the critical concentration 0.5 wt% of CTAB is shown in figure 2.

Standard pulse-echo technique(PET) has been used for ultrasonic absorption measurements at different frequencies. The ultrasonic intensity decreases exponentially with the path length. Thus the intensity at particular distance between the quartz crystal and the reflector in the experimental arrangement can be written as:

$$I_x = I_0 e^{-2\alpha x} \quad (1)$$

where x is twice the distance between quartz crystal and the reflector. I_0 is the maximum intensity and ' α ' is the absorption coefficient.

If I_{X_1} and I_{X_2} are the intensities of ultrasonic waves at X_1 and X_2 distances from quartz crystal then from Eq. (1) one can write the following expressions.

$$I_{X_1} = I_0 e^{-2\alpha X_1} \quad (2)$$

$$I_{X_2} = I_0 e^{-2\alpha X_2} \quad (3)$$

On solving the eqs. (2) and (3) one can easily obtain the following expression for the ultrasonic attenuation.

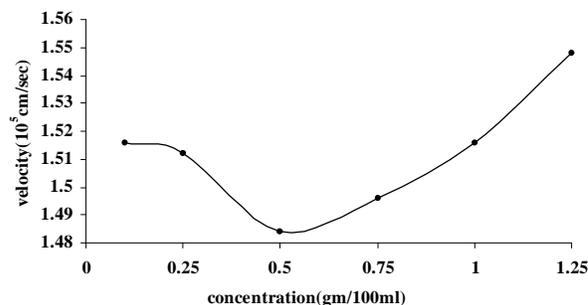


Figure 1: Velocity vs concentration at temperature 25°C

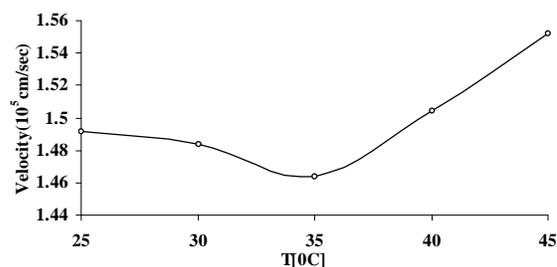


Figure 2 : Velocity vs temperature at 0.5wt% concentration of CTABr in decanol and water

$$\alpha = \frac{1}{2(X_2 - X_1)} \log \frac{I_{X_2}}{I_{X_1}} \quad (4)$$

The absorption coefficient is calculated using the eq. (4). Finally we obtain the values of ultrasonic absorption coefficient over frequency square (α/f^2). Accuracy in the absorption measurement is $\pm 5\%$. Several known values of ' α ' and ' V ' for standard liquids were justified so as to have satisfaction in absorption and velocity measurements. The observations were repeated several times.

We have measured the ultrasonic absorption from 25°C to 45°C at the frequencies 5MHZ, 15MHZ, 25 MHz and 35MHZ at different concentrations. The values of ultrasonic absorption coefficients (α/f^2) are shown in figures 3-6.

RESULTS AND DISCUSSION

Previous ultrasonic work on transition phenomenon had found the absorption coefficient maxima and velocity minima on temperature and concentration scale^[41]. The aim of present study was to see, whether the CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$) in decanol and water system show micelle formation^[42] or not. Firstly, the velocity measurements were being considered, as they are very accurate and to insure the over all behaviour of liquid crys-

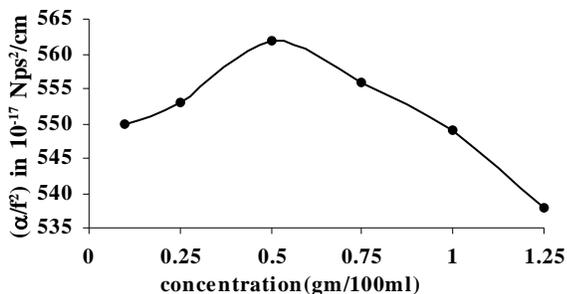
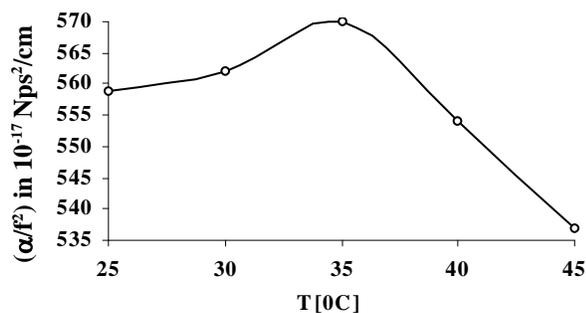
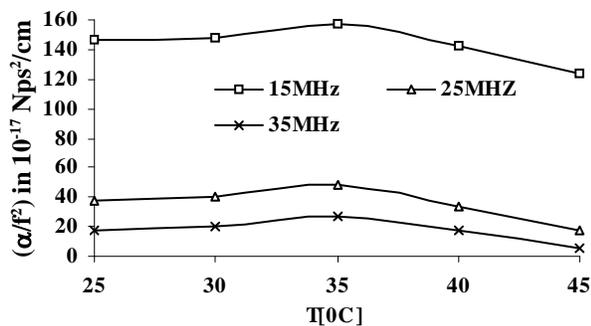
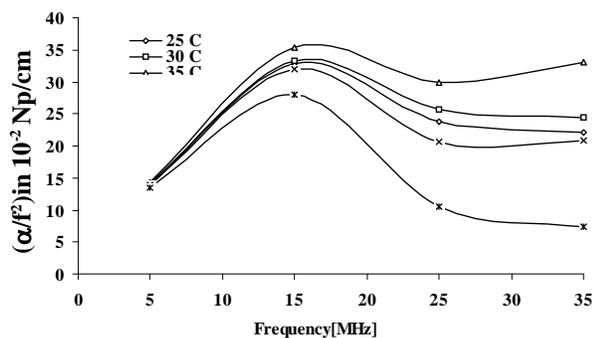
Figure 3: (α/f^2) vs concentration at 25°CFigure 4: (α/f^2) vs temperature at 5MHz and at 0.5 wt% of CTABr in water+decanol

Figure 5: Absorption vs temperature at 0.5gm/100ml of CTABr in water+decanol

Figure 6: Absorption (α) vs frequency

tal. The variation of ultrasonic velocity as a function of concentration at 2MHz and at 25°C has the characteristic velocity minimum at 0.5wt% of CTAB in decanol + water in figure 1. Next velocity measurements have been made at concentration 0.5wt% as function of temperature. The characteristic velocity minimum was observed at 35°C (Figure 2).

The variation of ultrasonic absorption over frequency square (α/f^2) with concentration at 5MHz and at 25°C (Figure 3) has the characteristic maximum for 0.5wt% of CTAB in decanol+water. Thus both the concentration dependent ultrasonic velocity and absorption (Figure 1 and figure 3) revealed a characteristic behaviour of the solution at 0.5wt% of the solute, called as critical concentration. The minimum in velocity also found its analogy in the velocity at the critical point in the binary liquids, which also has minima at critical points^[41].

The characteristic maximum at 35°C has also been observed in temperature dependent α/f^2 at the critical concentration for the different frequencies (Figure 4-5). Thus the temperature variation of ultrasonic velocity and absorption (Figure 2 and figures 4-5) determine, 35°C as the characteristic temperature for the solution, called as critical / transition temperature.

Anomalous behaviour of ultrasonic absorption and velocity in the present system at critical points is due to micelle formation. The micelle formation of this system at the critical points was also proved by the study of change in structural ordering and symmetries of the system^[42]. Hence, our work is justified.

The absorption maxima shift has been observed in the variation of ultrasonic absorption (α) versus the frequency (Figure 6) at different temperatures at the critical concentration. The shifts of peak were found in relaxational behaviour of molecular diffusion processes^[43].

α/f^2 is a constant quantity if only the contributions from shear viscosity are considered and the viscous relaxation does not occur. However, if a temperature dependent molecular process occurs in the solution, then pressure and temperature perturbation is introduced and a maximum interaction takes place at a certain characteristic frequency (f_c : relaxation frequency) at each temperature resulting absorption maxima at each temperature. An explanation of shifting of the maxima can be understood by taking place relaxational behaviour char-

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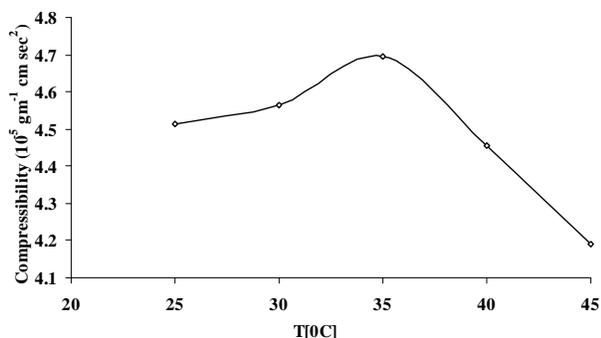


Figure 7: Compressibility (β) vs Temperature at 0.5 wt% CTABr in the solution

acterized by the frequencies greater than 15MHz and at the critical concentration. This may be due to the molecular association of the solvent and the solute by hydrogen bonding, but the details of the mechanism do not concern us in the present phenomenological consideration. The shifting of absorption maximum with relaxation frequency proves the spontaneous formation of micelle.

The adiabatic compressibility (β_s) is well related to the velocity of the ultrasonic wave ($\beta_s = 1/\rho V^2$). The evaluated adiabatic compressibility at different temperatures for the critical concentration (0.5wt%) of CTAB is shown in figure 7.

The behaviour of ultrasonic velocity gives information about the density and compressibility of the medium as they are well related.

$$V^2 = \frac{1}{\rho\beta_s} = \frac{\gamma}{\rho\beta_t}; \quad \gamma = \frac{C_p}{C_v} \quad \beta \equiv \text{Compressibility}$$

The temperature variation of adiabatic compressibility at critical concentration (Figure 7) has maximum at 35°C. This is due to the collapse of hydrogen bonding networks or a significant reduction of hydrophobic interactions at this temperature. The anomalous change in the adiabatic compressibility indicates about the formation of the liquid crystalline state^[44]. Thus the characteristic behaviour of adiabatic compressibility demonstrates the formations of liquid crystalline state at the critical concentration and the temperature in the present solution.

Phase transitions were inferred from the significant changes in slope in the conductivity (k) verses temperature plots^[44] of the liquid crystalline material. More precisely, the transition temperature is the point at which $(\partial k/\partial T)$ has maximum and $(\partial^2 k/\partial T^2)=0$. If we correlate

the temperature variation of the ultrasonic velocity/ absorption (Figures 1,4,5) and the temperature variation of the electrical conductance of the present system then phase transition at the critical point may be predicated with the plot of the temperature dependent electrical conductance of the present system.

The thermal stability and the ionic conductivity have minima at 35°C at the critical concentration for the binary mixture^[44]. Correlating the behaviour of the ultrasonic velocity of the present system with that of the thermal stability and the ionic conductivity of the binary mixture^[44], we may predict that thermal stability and the ionic conductivity of the present ternary system has minimum value at 35°C.

The nonaqueous solution formed by CTAB and ethylene glycol forms the lyotropic liquid crystalline state^[44]. The critical concentration and critical temperature for this nonaqueous solution were 6.5wt% and 15°C. The characteristic behaviour of the concentration and the temperature variations of the ultrasonic velocity and absorption has similar trend as in our case but has different magnitude. The ultrasonic velocity in the present solution has lower magnitude than for the solution formed by the CTAB and ethylene glycol, thus has larger absorption in comparison to that because for liquid and crystalline state $(\alpha/f^2) \propto V^{-3}$ ^[12-15]; where V is the velocity of ultrasonic wave.

Thus ultrasonic properties of the CTAB+decanol+water are very important to detect the liquid crystalline phase. Behaviour of the ultrasonic absorption / velocity at different conditions with other experimental findings reveals the qualitative information about the liquid crystalline phase appearing in the ternary mixture. Our ultrasonic technique is the simplest technique, which is non-radiative and non-destructive for the study. The results may be used in applications in industries for the purpose and further investigations.

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