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ACOUSTICAL PROPERTIES IN THE REGION OF PHASE TRANSITIONS IN THE AQUEOUS SYSTEMS OF LYOTROPIC MESOGENS

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Abstract The results of the acoustic investigation are reported for phase transitions in aqueous systems of rod-like and disc-like mesogens, forming the lyotropic mesophases of different types.

INTRODUCTION

The study of lyotropic liquid crystal systems has attracted a special attention lately, for the functioning of biosystems is based upon the principles of lyotropic mesomorphism. It also gives a unique possibility for investigating general properties and specific characteristics of phase transition, connected with the differences in the nature and the structure of mesophases.

Liquid crystals are characterized by a variety of phase transitions displaying both the first order as well as the second order natures. An acoustic method proved to be one of the most sensitive methods for studying the dynamical processes in the region of phase transitions. It has been widely used for an investigation of thermotropic liquid crystals.[1-3]

As a rule, the increase of times, specific for dynamic processes of this mesophases, is being observed with the approaching to the temperature of phase transition. The most informative in this aspect are investigations in the range of ultrasound low frequencies (below 1MHz). New possibilities in the study of phase transitions ap-

pear when investigating lyotropic liquid crystals (LLC). Not much information was published concerning physical properties of lyomesophases. Generally, the data were connected with the study of lyotropic nematics, which physical properties were found to be *qualitatively* similar to those of the thermotropic nematics. Though *quantitatively* these parameters, characterizing their properties, differ much from those of the thermotropic nematic phases.

In this paper we report the results of the acoustic investigations in aqueous systems of lyomesogens, capable of forming the lyotropic mesophases of different types.

MATERIALS AND METHODS

Lyotropic discotic mesogens 4,4',4'',4'''-tetrasulfated copperphthalocyanine [CuPht(4-SO_3H)$_4$] and 4,4',4'',4'''-tetracarboxylated copperphthalocyanine [CuPht(4-COOH)$_4$] were synthesized by a willer method.[4] Commercially available rod-like mesogen: decylsulfate Na (DSNa) was being recrystallized three times from ethanol till the $T_{m.p.}$ = 467 K.

A bidistilled water was used to prepare multicomponent aqueous systems.

The following systems made by gravimetrical method were used in the experiments:

1) CuPht(4-SO_3H)$_4$-NH_4OH-H_2O with the pigment concentration 30 wt.% , pH 11.0;
2) CuPht(4-COOH)$_4$-NH_4OH-H_2O with the pigment concentration 3 wt.% , pH 11.0;
3) DSNa-decanol-Na_2SO_4-H_2O (33.52:5.49:3.82:57.17 wt.% correspondingly).

Measurements of attenuation and relative changes of ultrasound velocity were done in cooling regime for the sample by pulse-phase method at frequency 3 MHz.[5] The sensibility of this method for measuring the ultrasound velocity was $\sim 10^{-3}$% and for the change of the attenuation $\sim$1-2 %.

An absolute value of ultrasound velocity was determined by measuring the time of a signal passing through the cell with an accuracy to $\sim$ 1 %.

The value of the attenuation was calculated relatively to the free distilled water. In micellar system DSNa-decanol-Na_2SO_4-water the measurements of velocity and attenuation were carried out by an acoustic resonator method in the region of 0.3 - 1.2 MHz.
This method of measuring is discussed in detail in the work.[6] It should be mentioned that we did not fix experimentally an anisotropy of acoustic parameters of the solutions studied at reorientation of the external magnetic field B = 0.8 T relatively to the wave vector. Therefore all the material, given below, belongs to the non-oriented specially LLC samples.

RESULTS AND DISCUSSION

The aim of this work was to study the temperature variations of ultrasound velocity and the attenuation α of longitudinal ultrasound change in the systems chosen by us.

In the figure 1 the temperature dependence of ultrasound velocity at frequency 3 MHz is represented. The temperature dependence of ultrasound velocity in distilled water is also given in the same picture at this very frequency.
It is known that free water has a lot of anomalous physical properties. One of them is a completely different character of temperature dependence of ultrasound velo-

city if compared to others. This velocity grows when increasing the temperature, reaching its climax at $t^{\circ} \approx 74^{\circ}C$, and then goes down if the increase of the temperature is proceeded. This peculiarity of the temperature dependence of ultrasound velocity in free water

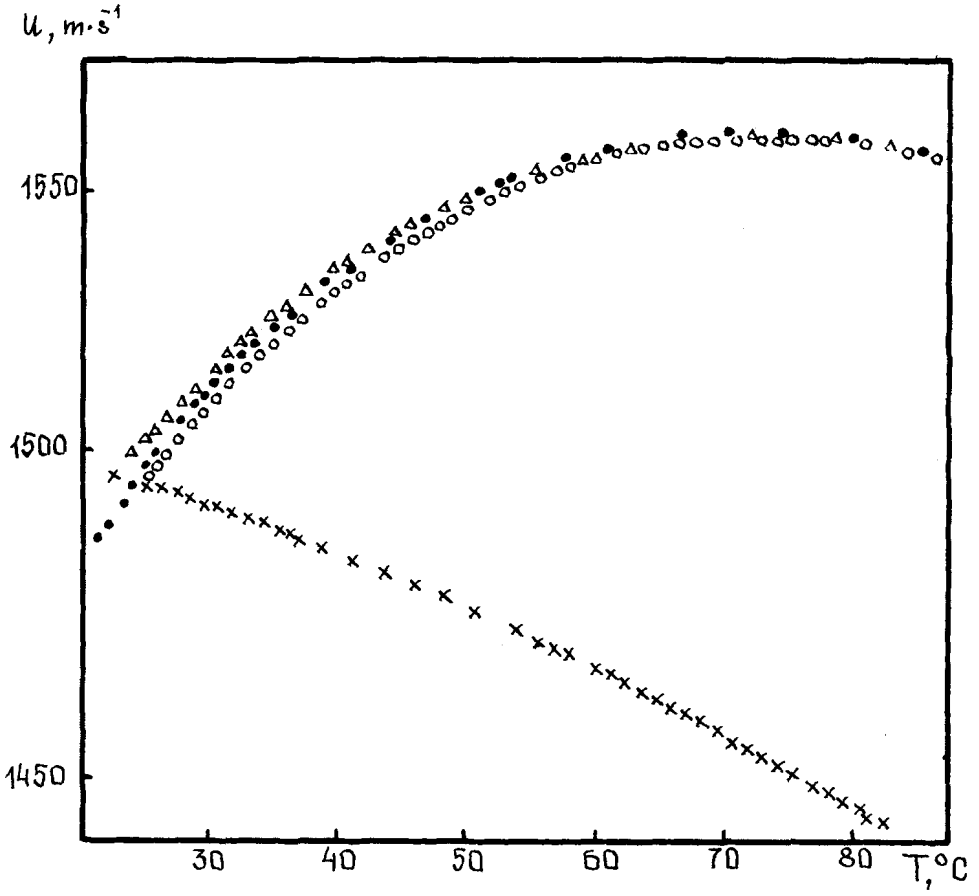

FIGURE 1 Temperature dependence of the ultrasound velocity (f = 3 MHz):
- • free water,
- ▲ CuPht(4-SO_3H)-NH_4OH-H_2O system,
- o CuPht(4-COOH)$_4$-NH_4OH-H_2O system,
- x DSNa-decanol-Na_2SO_4-H_2O system.

is also a characteristic feature of investigated solutions of copperphthalocyanine sulfo- and carboxy-derivatives, capable of forming lyomesophases of chromonic type. The identical character makes us presuppose that the influence of soluted compounds and their supermolecular aggregates on the elastic parameters of solutions is not big. It is also possible to make a supposition that the compressibility of studied solutions of copperphthalocyanine derivatives is determined first of all by the hydration water of molecules and molecular aggregates, i.e. their solvatation.

Actually, the forces of this interaction are likely to be short functioning and therefore a noticable influence of molecular aggregates on elastic characteristics of the solvent cannot be expected.

Evidently, the molecules of a solvat layer are not substantially connected with the supermolecular aggregates and the influence of the latter mostly displays in the change of a translation mobility of the water molecules closest to them.

The character of temperature dependence of ultrasound velocity totally different from the previous one, was found in the DSNa-decanol-Na_2SO_4-water system, which may form supermolecular *micellar* structures of amphiphilic molecules. In this case the anomalous properties of free water, connected with the distributive velocity of longitudinal acoustic waves are not displayed: the ultrasound velocity decreases monotonously when increasing the temperature.

In the figure 2 the temperature dependences of attenuation (α/f^2) are given, where f is ultrasound frequency. One can see from the picture that α/f^2 decreases in the studied solutions when increasing the temperature and does not have any anomalies in the region of phase transitions.

The exception are the results obtained in a low fre-

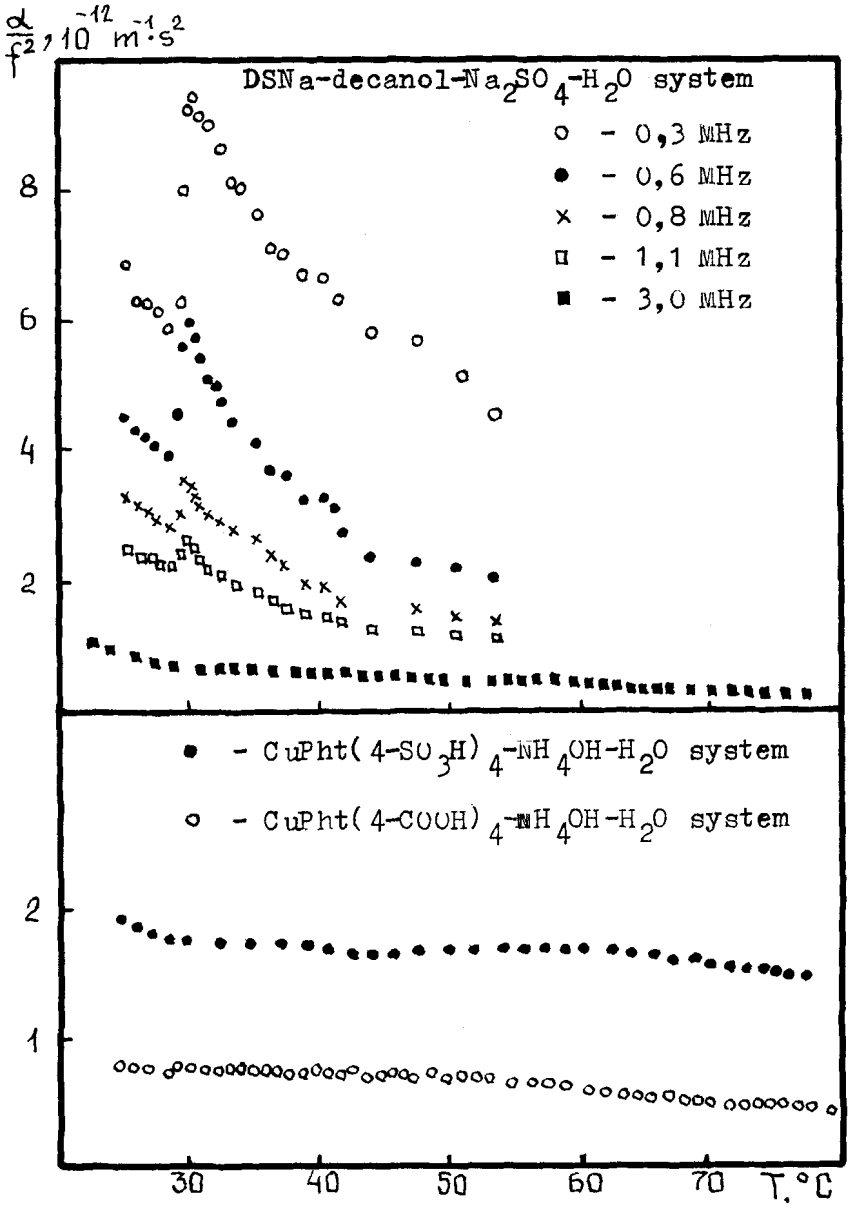

FIGURE 2 Temperature dependence of the attenuation.

quency range of a micellar system, where the attenuation reaches its climax at the $T \approx 31^{\circ}C$. We connect the aforesaid anomaly with a structural transition

$N_d \dashrightarrow N_c$ which has been found by us before.[7] The attenuation data depend in this case on ultrasound frequency in the whole studied temperature interval. Corrections to the attenuation, conditioned by the transition, depend upon the ultrasound frequency and become rather low at $f > 1$ MHz.

It means, that the relaxation times' interval of specific dynamic processes, connected with the transition mentioned above, is much higher in comparison with the times of the dynamic processes at phase transitions of thermotropic nematic phases. It is difficult to carry out a *quantitative* analysis of the data, obtained on the basis of a temperature dependence of the ultrasound attenuation, for the values of corrections to α/f^2 are too small in the frequency interval used by us. For kind of quantitative analysis like that and in order to compare the obtained data with the results of ultraacoustic investigations of phase transitions in thermotropic liquid crystals, we have to carry out some measurements in a lower frequency region, which is not experimentally available for us at the moment.

The regular character of temperature dependence of ultrasound attenuation in the temperature region, corresponding to the phase transition to isotropic state proves again a supposition that the character of a temperature change of viscous-elastic parameters in the studied systems is mostly determined by the change of solvent parameters.

In the figure 3 the results of a measurement of the relative changes of velocity and the attenuation in the $CuPht(4\text{-}COOH)_4$- solvent system are given at a fixed $T = 24^oC$ when the pigment concentration was being varied. As it is possible to see from the picture, the ultrasound velocity curve in this system goes up when increasing the concentration, having a sudden leap at $c = 2,8$ wt.% of $CuPht(4\text{-}COOH)_4$ and the attenuation starts noticably changing at this very con-

centration. We connect this leap of an ultrasound velocity with the I ⟶ N phase transition.[8] This spasmodic change of the value is conditioned by the increase of mesophase compression which is specific for a phase transition of the first order. The remarkable increase of the attenuation in the mesophase supposedly may be connected with a contribution of an extra absorption mechanism specific for an anisotropic liquid : contributions from the relaxation of order parameter's modul, its fluctuations and others.

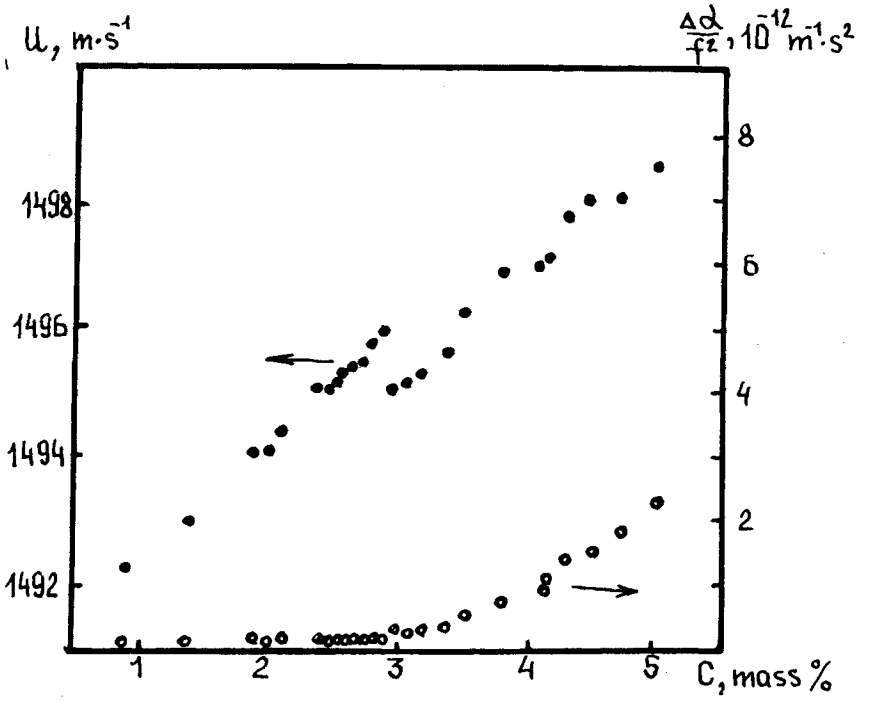

FIGURE 3 Temperature dependence of the velocity and attenuation in the $CuPht(4\text{-}COOH)_4\text{-}NH_4OH\text{-}H_2O$ system on the concentration of the pigment, f = 3 MHz.

Thus, as a result of this work, the acoustic parametres of different lyomesophases were obtained. It is for the first time that the quantitative analysis of phase transitions in lyomesophases of discotic mesogens was carried out.

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