Relative permittivity behavior and temperature changes in linoleic acid during the phase transition.

R Kościesza, R M Siegoczyński, A J Rostocki, D B Tefelski, A Kos, and W Ejchart
Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, POLAND.
E-mail: raphael@if.pw.edu.pl

Abstract. In our earlier works several fatty liquids (edible oils and unsaturated fatty acids) which exhibit existence of a new phase induced by high pressure were presented. Conclusion of those experiments is that C=C bonds existence in these liquids plays a dominant role in a new phase occurrence. Relative permittivity in pure acids investigated till now seems to behave in specific way. That is why we decided to investigate linoleic acid (C_{18}H_{32}O_{2}) under high pressure. In our experiment such quantities as: electric capacity, pressure and temperature were recorded. The experimental setup gives us also a possibility to conduct optical investigations. We observed a transmitted and scattered beams of close infrared light ($\lambda = 800$nm) in directions $0^\circ$ and $90^\circ$ towards the incident beam. Due to the rapid grow of temperature and the rapid change of transmitted and scattered beams we may say that observed phenomenon is a first order phase transition and a proof for the significant change of liquid structure. This paper contains time dependencies of permittivity, temperature, transmitted and scattered light intensity and also permittivity vs. pressure changes during the phase transition in linoleic acid and first of all measured data analysis which lets us explain the transition reasons.

1. Introduction
Conclusions that we came to in experiments with oleic acid and other fatty liquids showed us that investigations of liquids which contain C=C bond have a reasonable basis. Their increasing role in food and petrol industry and medical application (its isomers prevent breast and colon cancer [1]) is just another reason to keep investigations on. In this paper we are especially interested in the linoleic acid. It is one of unsaturated fatty acids. As well as in liquids investigated by us till now we can induce a high-pressure phase transition in linoleic acid too. We can observe occurrence of the new phase by measuring the scattering light and the temperature inside the chamber. There are no significant changes of the relative permittivity which lets us to conclude that we deal with a transition of investigated medium to the new phase. We have investigated a few fatty acids and the insignificant changes of electric permittivity[2] seems to be characteristic in general.

2. Experiment
The pressure in our high pressure apparatus is generated by piston-cylinder system with multiplication. This system is supplied by a computer-controlled pump with regulated velocity of pressure application. The chamber has three sapphire windows for optical investigations. Optical signal from the modulated, infrared pin diode is registered by two detectors. Then it is conditioned in
lock-in and amplifier. The source wavelength is well-chosen to avoid molecular absorption and to be well transmitted by the sapphire windows. Electric quantities such as capacity, voltage (from copper-constantan thermocouple and light detectors) and resistance (from manganin coil) are measured by multimeter and RLC bridge. All data obtained during the experiment is collected and converted by acquisition system designed in our lab.

3. Results
As it was shown in an earlier paper [3], a new high pressure phase occurs in linoleic acid. Main pointer of phase transition is a rapid increase of a scattered light and rapid decrease of transmitted light simultaneously. Such case is shown in figure 1. This paper considers relative permittivity and temperature behavior during the phase transition. Changes of these parameters are presented in figure 2.

Comparing the light and permittivity-temperature graphs we may notice that sudden changes of beams intensity are correlated with rapid temperature changes. Small changes of relative permittivity during the transition were observed. Linoleic acid is a dipole liquid that was placed in electric field during the experiment. Figure 2 exemplifies thermal effects on electric dipoles mutual orientation. At the begging of the phase transition increase of temperature destroys parallel orientation of single, free dipoles which are turned according to the electric field. Random orientation of dipoles leads to a decrease of total dipole moment and decrease of the relative permittivity. During the return to the initial phase temperature decreases and free dipoles align according to the electric field again. Analysis of the relative permittivity changes was our main tool which let us to investigate phase transitions in fatty liquids [4-8]. To find out more about the phenomenon that we deal with, the authors decided to consider investigated liquid using the Fröhlich theory of dielectrics [9]. Such analysis seems to be the most reasonable one, for it gives the best view on squared average macroscopic dipole moment in our liquid, which depends on the relative permittivity changes that is correlated with pressure [10]. This relation is described by equation 1.

\[
<\langle \text{m} m^* \rangle> = \frac{3\varepsilon_0 kT(\varepsilon(p) - \varepsilon_\infty) (2\varepsilon(p) + \varepsilon_\infty)}{3\varepsilon(p)N(p)}
\]

<\langle \text{m} m^* \rangle> is an average product of the dipole moment \textbf{m}^* of single cell of Fröhlich cavity and the whole cavity dipole moment \textbf{m}, \varepsilon is a relative permittivity, \varepsilon_\infty can be approximated as a squared refractive index of the linoleic acid, N is molecules concentration per volume unit. The figure 3 presents structural factor <\langle \text{m} m^* \rangle> and molecules concentration changes during phase transition.
Total dipole moment is decreasing while concentration of molecules in capacitor is still increasing. It leads to insignificant changes of relative permittivity in time of the transition. Small decrease of $\varepsilon$ during transition is caused by earlier mentioned thermal influences and dipoles interactions. In spite of the electric dipoles mutual interactions play insignificant role in mechanism causing the phase transition we may observe the loop of hysteresis (figure 4), which proves that some of them turned anti-parallel one to each other during the whole compression-decompression cycle. Width of loop of hysteresis is proportional to the number of free electric dipoles that are not creating dimers with other molecules of acid. In our case, the structure of liquid is changing but its electric properties are kept. Strong scattering state and visible temperature changes are our main pointers of a new phase occurring. All our measurements were done in the room temperature. From thermodynamic point of view we had foster conditions for rapid grow of a scattering centers composed of interacting acid molecules [11]. As in the case of oleic acid these centers may be structures of short range order similar to the smectic phase in liquid crystals [12]. Such crystal-like structures have other refractive index and density than surrounding liquid. Number, diameter and packing of the crystalites grow due to pressure increase, and this situation forces the change of acid compressibility (figure 5).

Figure 3. Structural factor and molecules concentration during phase transition.

Figure 4. Change of relative permittivity in compression – decompression cycle.

Figure 5. Time dependency of the pressure.

In this figure we can clearly see the changes of the compressibility by observing the pressure curve slope. Every change of slope in time of compression as well as decompression means change of compressibility and packing of crystalites. What is more interesting is that there are no visible changes of scattered and transmitted light intensity according to the changes of optical properties of investigated medium. Due to compression, liquid is getting more dense so the crystalites do not grow
any more, optical signal falls and finally it is getting stable. Multiple light reflections and multiple scattering inside the chamber attenuate the optical signal.

4. Conclusions
First order phase transition in linoleic acid was observed. New high-pressure phase occurrence is strongly correlated with scattered light and temperature increase. The most interesting thing is that no significant changes of electric permittivity were noticed, what is well explained using Fröhlich theory of dielectrics. High pressure treatment of linoleic acid is causing significant structure changes at molecular level. It leads to creating the scattering centers structure of which is similarly ordered as in liquid crystals smectic phase. As it is shown in figure 5 there are few intermediate states which have different physical properties such as compressibility and pacing of molecules.

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