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The investigation of the dynamics of the phase transformation in triolein and oleic acid under pressure

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Abstract. An aim of our work is the understanding of processes happening during phase transformations under the pressure in triglycerides and unsaturated fatty acids. Particles of investigated liquids possess the double bond between carbon atoms, which causes the bended shape of the particle and makes its free rotation impossible. This property causes low temperatures of melting point and high temperatures of boiling and also investigated by us phase transformations. For study of the dynamics of phase transformation in these liquids we measured light transmission and light scattering at 90 degrees angle, temperature, permittivity and internal pressure versus time. We applied pressure using computer controlled pump with a stepping motor, which makes increase of the pressure steady. The phase transformation in oleic acid lasts several seconds, in triolein it lasts several minutes. We think that the elongated time of phase transformation is caused by a hooked shape of particles of triolein and the dynamics of that process is determined by the tangling of particles. We checked the influence of smaller particles of oleic acid on the phase transformation by investigating the mixture of these liquids.

1. Introduction
Interesting phase transformations firstly were found in castor oil [1, 2]. Formally optical observation were the first where such phenomena was observed, then they were followed by the other observations like temperature changes, permittivity, volume changes, x-ray diffraction [3]. Understanding processes which occur during high pressure treatment of compounds of oils is very important because of its meaning in food and fuel industry. Observations which were performed and described in [4] have been repeated with much higher precision. Data acquisition and control of experiments are now fully automated. Pump with stepping motor allowed us to apply pressure in very accurate way. Light transmission and light scattering [5] studies lead us to pay attention to rod-like compound models such as, for example presented in this work [6].

2. Measurement configuration
Our experiments were performed with use of high pressure optical chamber. This steel chamber has three optical entrances which are made of sapphire cylinders in configuration, allowing light observation in transmission geometry and at 90 degrees (scattered light). The windows are sealed using Bridgeman sealing system with use of brass gaskets. There is also an electrical interface which also uses Bridgeman sealing. The high pressure electrical interface has several thin wires which are wound on thread cone-shaped element and filled with epoxy resin. Inside the chamber there is a cylindrical space which is filled with examined liquid. Sensors like thermocouple,
manganine wire pressure sensor and capacitor for dielectric permittivity investigation are placed there. A simple piston moves in this space causing pressure increase in the examined liquid. A force is transmitted by pressure multiplication device mounted on top of the pressure chamber which is based on a different diameter of pistons. The pressure multiplication index is 25. The pressure at low values (up to 30MPa) is generated by pressure pump driven by stepping motor which is controlled by computer. This provides the steady increase of the pressure. Sensors from high pressure chamber are connected to corresponding measuring devices. Capacitor is connected through the high pressure interface by four wire method to an precision LCR meter (HP4284A). Thermocouple is connected to digital multi-meter (DMM) with multiplexed input (HP34970A) through a device providing constant temperature for a second thermocouple terminal. This provides a precision of temperature measurement, regardless of ambient temperature variations. A manganine wire in form of coil is also connected to input of HP34970A. Our experiment set has optical devices: Infrared Sender device with IR LED ($\lambda = 800\text{nm}$), two Infrared Receivers with p-i-n photo-diodes, lens for focusing scattered light and a modular phase–sensitive detection system. This phase–sensitive detector (Lock-in) built on Faculty of Physics Warsaw University of Technology makes an SNR (Signal to Noise Ratio) high increase and high stability in long time observations in presence of external disruptions possible. For Lock-in adaptation, emitted light is modulated with frequency of 2931Hz. The wavelength (800nm) of emitted light was chosen specially to avoid molecular absorption. Because the intensity of scattered light was very small the positive lens was used to focus light on the detector photo-diode. The Lock-in system is connected with HP34970A. Both measuring devices: HP4284A and HP34970A are controlled via GPIB Bus by data acquisition system on personal computer with National Instruments LabVIEW software, which is prepared for long term acquisition, necessary in some classes of examined liquids. Permittivity was measured in similar way to the one described in [7]. Complete acquisition system is presented in figure 1.

3. Measurement conditions
Experiments are performed in standard conditions with ambient temperature $t_c = 25^\circ \text{C}$, ambient pressure of $P_a = 101.325kPa$ and relative humidity of $RH = 40\%$. Data from all sensors is

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Figure 1. Measurement system
collected in a period of 2 seconds. Capacitance was measured using Auto Balancing Bridge Method. A frequency used in this method was 1kHz and the amplitude of measurement signal was 1V. The examined liquids were chemically pure. For a mixture, liquids were mixed in magnetic stirrer. Before the experiments, the samples were stored in cool and dark place for preventing them from degradation.

4. Examined liquids
Triolein \((C_{17}H_{33}COO)_{3}C_{3}H_{5}\) is a triglyceride and unsaturated fat. It consists of flat type molecule of glycerine and three rod like molecules of oleic acid. It has a hooked shape. Oleic acid \(CH_{3}(CH_{2})_{7}CH=CH(CH_{2})_{7}COOH\) is a mono-unsaturated omega-9 fatty acid with rod-like shape bended on double bound. Triolein and its mixtures with methyl alcohol were examined in works \[8, 9, 10\], but not in optical chamber. Oleic acid was examined in works \[11, 12\].

5. Experiment progress
During experiment we increased the pressure with constant speed of piston displacement. We used stepping motor with 60Hz which is about 0.25MPa/s, 120Hz which is about 0.5MPa/s and 240Hz which is about 1MPa/s. The pressure was increased to 450MPa in examined liquid, and then we waited till all measurable parameters changed. After that, the pressure was decreased with the same speed. Data with light transmission, scattered light and pressure is shown in figure 2 for pure triolein and figure 3 for pure oleic acid. All experimental data from sensors were collected simultaneously by automated acquisition system.

![Figure 2](image-url)  \(\text{(P)}\) Pressure change, \((T)\) light transmission, \((S)\) scattered light at 90\(^\circ\) versus time in triolein \(v=120Hz\) (0.5MPa/s)

![Figure 3](image-url)  \(\text{(P)}\) Pressure change, \((T)\) light transmission, \((S)\) scattered light at 90\(^\circ\) versus time in oleic acid \(v=120Hz\) (0.5MPa/s)

6. Observation
In figure 4 we see large optical hysteresis. A noticeable fact is that when we add more then 25\% oleic acid to triolein, when phase transformation begins the pressure tends to decrease. We can also see different character of light transmission changes in triolein and in oleic acid. Phase transformation in triolein took much more time as in oleic acid and it begins slowly with distinct slope. Phase transformation in oleic acid begins abruptly and the beginning slope is very slight. The dependence of the transmitted light on gradually applied pressure was discussed in paper \[13\]. According to the Mie’s theory, strong decrease of light transmission is connected with an increase of the sizes of the light scattering objects. It is because particles accumulate and build up inceptions of new structure. Such new clustered objects cause increased scattering,
which is visible on scattered light at $90^\circ$. Later because of solidification, both transmitted and scattered light diminishes. In pure triolein, there is a characteristic slow scattering light decay in similar shape like in the pressure curve. In all mixtures of triolein and oleic acid and in all examined speeds we did not observe such elongated scattered light behavior. It can be explained that phase transformation (creation of inceptions of new structure) of oleic acid masks the phase transformation behavior of triolein. Simply it begins earlier. Leaving light changes out of account, the pressure changes show the moment of original structure breakdown. In triolein this happens when compression stage is completed and we just wait (time near 3000s in figure 2). In oleic acid it is visible during compression stage at about 150MPa pressure (time near 1000s in figure 3).

![Figure 4. Light transmission versus pressure. Labels with 1 - pressure increase, with 2 - pressure decrease. A - triolein, B - triolein + oleic acid 75:25, C - triolein + oleic acid 50:50, D - oleic acid.](image)

![Figure 5. Logarithm of light transmission in pure triolein and fitted lines to fragments representing two relaxation times in Edwards model of motion in potential and "hopping". Slopes are inverse negative $\tau_1$ and $\tau_2$.](image)

7. Applying the model
We have considered using the Edwards [6] model of rod-like compounds to this group of liquids. So after light transmission observation we choose two characteristic parameters from light transmission. They appear to behave as exponential decay. We have fitted line functions to logarithm of light transmission and obtained slopes corresponding to harmonic move in the potential $\tau_1$ and "hopping" $\tau_2$ which is time characteristic for opening and closing gates as obstacles in compound movement. Then having this parameters, we calculated the $\alpha$ parameter which is related with Kramer’s probability of escape and further is a part of diffusion equation. According to the Edwards calculations, diffusion is connected with $\alpha$ parameter by $D = D_0 \left(1 - \frac{\alpha}{\tau_1}\right)$ and $\frac{2\alpha}{\tau_1} = \frac{1}{\tau_2} \alpha$ which transformed is $\alpha = \frac{-\tau_2}{\tau_1 + \tau_2}$. Therefore slopes from fitted lines $(y = ax + b)$ to logarithm of light transmission (which is shown in figure 5 are inverse negative $\tau_1$ and $\tau_2$ parameters. $\tau_1 = -\frac{1}{\alpha_1}$, $\tau_2 = -\frac{1}{\alpha_2}$. After calculations, obtained parameters are shown on table 1. The $\alpha$ parameter versus speed of applied pressure for triolein, oleic acid and their mixtures is presented in the figure 6.

8. Conclusion
It is interesting that the $\alpha$ parameter decreases proportionally to speed of applied pressure. It has the highest value for pure triolein and tends to have the smallest value for pure oleic acid, so diffusion in triolein is the smallest and diffusion during phase transformation tends
Figure 6. $\alpha$ parameter versus speed of pressure change.

Table 1. $\tau_1$, $\tau_2$, $\alpha$ parameters and their uncertainties obtained from fitting linear functions to fragments of logarithm of light transmission in examined liquids at particular speed of applied pressure.

| Examined liquid                      | $\tau_1$ [s] | $\Delta \tau_1$ [s] | $\tau_2$ [s] | $\Delta \tau_2$ [s] | $\alpha$   | $\Delta \alpha$ |
|--------------------------------------|--------------|---------------------|--------------|---------------------|------------|-----------------|
| Triolein v=60Hz                      | 4710         | 20                  | 35.2         | 0.2                 | 0.00741    | 0.00006         |
| Triolein v=120Hz                     | 2680         | 20                  | 15.22        | 0.06                | 0.00565    | 0.00007         |
| Triolein v=240Hz                     | 3100         | 200                 | 8.79         | 0.05                | 0.0028     | 0.0002          |
| Triolein + oleic acid 75:25 v=60Hz   | 10270        | 60                  | 27.21        | 0.07                | 0.00264    | 0.00002         |
| Triolein + oleic acid 75:25 v=120Hz  | 8670         | 60                  | 13.3         | 0.1                 | 0.00153    | 0.00002         |
| Triolein + oleic acid 75:25 v=240Hz  | 8200         | 300                 | 6.7          | 0.1                 | 0.00081    | 0.00004         |
| Triolein + oleic acid 50:50 v=60Hz   | 5940         | 40                  | 10.4         | 0.2                 | 0.00175    | 0.00004         |
| Triolein + oleic acid 50:50 v=120Hz  | 20000        | 5000                | 6.63         | 0.01                | 0.00033    | 0.00008         |
| Triolein + oleic acid 50:50 v=240Hz  | 15600        | 600                 | 3.73         | 0.04                | 0.00024    | 0.00001         |
| Oleic acid v=60Hz                    | 6130         | 20                  | 10.2         | 0.1                 | 0.00167    | 0.00003         |
| Oleic acid v=120Hz                   | 6900         | 200                 | 4.90         | 0.07                | 0.00071    | 0.00003         |

to increase within faster pressure applying. So this shows that movement of more complex hook-shaped compound like triolein is harder than simpler rod-like compound like oleic acid. Addition of oleic acid increases mobility in such mixture, because there is more space between complex compounds which tend to entangle. Also we see that addition of oleic acid changes behavior of observed scattered light dramatically, so the dynamics of phase transformation of such configuration changes and oleic acid phase transformation tend to mask triolein behavior. Generally as a basis of approach towards diffusion, we used speed of appearing and growing of the scattering objects as a dependency of pressure. Further research in this direction is legitimate. Exploiting the Edwards model should be verified in other conditions like temperature dependence.
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