High Pressure Changes of the Castor Oil Viscosity By Ultrasonic Method

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Abstract. The pressure change of viscosity of castor oil have been measured by ultrasonic method within the range of pressure up to 0.9 GPa. For the measurement, the authors have applied a new ultrasonic method based on Bleustein-Gulyaev (B-G) waves. For the lower pressures (up to 0.3 GPa) the results have been compared with earlier results obtained by falling body method, whereas for the higher pressure range results were compared with those obtained by the flow type viscometer. The measurements have shown: 1. Exponential rise of viscosity with pressure up to 0.4 GPa according to the Barus formula. 2. Extraordinary increment of viscosity at constant pressure during phase transition. 3. The decomposition of the high pressure phase during the decompression process have shown very large hysteresis of viscosity on pressure. 4. After the decompression process the viscosity lasts higher then a initial value for several hours.

1. Introduction
The aim of this paper was: 1. To test the new ultrasonic method of viscosity measurement based on Bleustein-Gulyaev waves at the high-pressure conditions. 2. To compare the results with the results of viscosity on pressure measurements of castor oil obtained by other methods. 3. To observe the isobaric changes of castor oil viscosity during the phase transition process. 4. To measure the viscosity of high pressure phase of castor oil. Castor oil was one of the most extensively examined under high pressure natural oils, for its wide use in some laboratories as a pressure transmitting medium in dead-weight piston gauges for the range up to 1 GPa [1]. For this reason its rheologic properties were investigated in limited range several years ago [2, 3]. It was also a subject of our investigation since the beginning of our works. The strong, exponential dependence of viscosity on pressure known in the literature as “Barus formula” suggested that the small difference in the composition of liquid might cause the big difference of the viscosity at high pressure. For investigation of those effects the high pressure viscometer of the falling ball type with rotating pressure chamber up to 1.5 GPa and electronic time measurement system has been built [2]. Although the pressure range of the chamber was up to 1.5 GPa, the measurement of viscosity of castor oil was limited to about 300 MPa (above that pressure the ball was not falling dawn at all). In 1986-87 the high pressure phase transition in castor oil was observed [4, 5]. The results of measurement of refractive index [6], compressibility [7], and dielectric permittivity [8] suggested that new high pressure phase of castor oil should also have significantly higher viscosity. Since the falling body method did not give the result for the pressure range above 300 MPa the
flow type method based on the Hagen-Poiseuille’s rule has been applied [9, 10, 11]. The new high-pressure phase of castor oil was found to be strongly non-Newtonian liquid. Thus the viscosity obtained from Hagen-Poiseuille’s relation was giving only effective (apparent) viscosity. In such case the complete rheological characteristics should be found what makes all measurement very complicated. Moreover all those complications made the measurement during phase transition process almost impossible. In this situation various ultrasonic methods were considered and finally the one based on Bleustein-Gulyaev waves was applied for the new measurement of castor oil viscosity.

2. Viscosity measurement using B-G waves

The Bleustein - Gulyaev (B-G) wave is a shear horizontal acoustic surface wave having only one component of mechanical displacement, parallel to the propagation surface and perpendicular to the direction of propagation. The energy of the B-G wave is concentrated in the vicinity of the waveguide surface. The viscoelastic liquid covering the waveguide surface loads it mechanically. The mechanical impedance of a layer of liquid loading the surface of the B-G wave waveguide is equal to the characteristic shear impedance of the liquid 

$$Z_L = (\rho_L \cdot G_L)^{1/2}$$

where 

$$G_L = G' + jG''$$

is the complex shear modulus of the liquid defined as the ratio \((T/S)\) of the shear stress \(T\) to the shear strain \(S\). \(\rho_L\) is the liquid density and \(j = (-1)^{1/2}\). In general, liquid loading of the sensor surface changes the phase velocity \(v\) and the attenuation \(\alpha\) of the B-G wave. The complex propagation constant \(\gamma\) of the B-G wave changes:

$$\frac{\Delta \gamma}{\beta} = \frac{\Delta \alpha}{\beta} - \frac{\Delta v}{v_0}$$

where \(\gamma = \alpha + j\beta\), \(\beta = \omega/v\), \(v_0\) is the phase velocity of the nonperturbed B-G wave on the free surface, and \(\omega\) is the angular frequency of the B-G wave. One can prove that the change in the complex propagation constant \(\gamma\) of the B-G wave produced by viscoelastic liquid loading is as follows [14, 15]:

$$\Delta \gamma = -j \left( \frac{|v_3|^2}{4P} \right) Z_L = -j K Z_L$$

where \(v_3\) is the B-G wave amplitude on the waveguide surface \((x_2 = 0)\), \(P\) is the mean power on the unit width of the B-G wave, \(K\) is the characteristic quantity for each B-G wave waveguide and depends solely on the material parameters of the waveguide and frequency. Knowing the change in the complex propagation constant \(\Delta \gamma\) from the experiment, we can calculate the complex shear impedance of the liquid \(Z_L = R_L + jX_L\). Subsequently by separating the real and imaginary parts of Eq.(1), we obtain the following components of the complex shear modulus of the liquid:

$$G' = \frac{R_L^2 - X_L^2}{\rho_L}$$

$$G'' = \frac{2R_L X_L}{\rho_L}$$

In the next step, the rheological model describing the investigated liquid should be determined. Using the chosen model and Eqs.(4) and (5), we came to the formulas for shear elasticity \(\mu\) and viscosity \(\eta\) of a viscoelastic liquid.

$$\mu = \frac{(R_L^2 + X_L^2)^2}{\rho_L \left( R_L^2 - X_L^2 \right)}$$

$$\eta = \frac{(R_L^2 + X_L^2)^2}{2\rho_L R_L X_L \omega}$$
3. Experimental set up

The real advantage of the method presented here is that contrary to the other methods of the viscosity measurement it does not require any special high-pressure equipment. Any high pressure equipment which can contain the ultrasonic B-G transducer can be used. In our case it was a rectangular bar of PZT type zirconium ceramics covered at one side with 200µm layer of silver at one side with a piezoceramic transducer bonded at the end of ceramics. The size of it was 6×10×40mm. The pressure was generated in a thick-walled cylinder of 17 mm internal diameter with a simple piston detaily presented in [16]. This piston-cylinder system was operated by a 20-tonne laboratory hydraulic press, what limited the maximum pressure to about 1 GPa. For pressure measurement, a typical 500Ω manganin transducer was used. Its resistance was measured with a precision HP 34970 multimeter. Pressure measurement accuracy was better than 0.1%. The experiments were done at room temperature. Temperature was measured by the copper - constantan thermocouple placed inside the chamber. For measuring viscosity using B-G wave [15], the sending - receiving piezoelectric transducer was driven by the TB-1000 pulser - receiver computer card. The B-G wave impulse generated by this transducer was reflected in multiple ways between two opposite edges of the piezoceramic waveguide. The signals received by the transducer were amplified by the pulser -receiver card and sent into PDA-500 digitizer card. This card sampled and digitized the input analog signals. The stored signals were then analyzed by computer software. For each measurement, the ultrasonic signal was averaged 1024 times in order to improve the signal-to-noise ratio. A computer program which controls the set-up operation was written in C++ language. Time of flight of the ultrasonic pulses was evaluated by applying the cross - correlation method.

4. Results of the measurement

The pressure was generated by the hand operated pump in 20 MPa steps then kept constant for about 2-5 minutes. During that time the pressure was carefully observed. That allowed to identify pressure drop due to the first order phase transition to observe whether the system is reaching thermodynamic equilibrium. After approaching 0.6 GPa the pressure was kept constant for about 20 hours to enable the phase transformation. During the phase transition the small drop

![Figure 1. Pressure changes of castor oil viscosity measured by B-G ultrasonic waves method.](image-url)
of pressure and big increment of viscosity was observed. The results of the viscosity measurement are shown in figure 1. As one can notice the results up to about 400 MPa are almost tangential to the exponential curve which represents Barus formula $\eta = \eta_0 \exp(\alpha p)$. Above 400 MPa the experimental points are rising slower than the theoretical prediction. Finally at 600 MPa when the pressure rise was stopped for about 20 hours the viscosity has risen to the new value characteristic for the high pressure phase of castor oil. The further increment of viscosity was rather linear function of pressure.

5. Conclusions
1. Exponential rise of viscosity with pressure up to the phase transition at 0.6 GPa according to the Barus formula. 2. Extraordinary increment of viscosity at constant pressure during phase transition. 3. The decomposition of the high pressure phase during the decompression process have shown very large hysteresis of viscosity on pressure. 4. After the decompression process the viscosity lasts higher than the initial value for several hours.

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