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Investigation of Ultrasonic Emulsifying Processes of a Linseed Oil and Water Mixture

Andrzej SKUMIEL[(1)], Arkadiusz JÓZEFCZAK[(1)], Krzysztof HELLER[(2)], Tomasz HORNOWSKI[(1)], Katarzyna WIELGUSZ[(2)]

[(1)] *Institute of Acoustics, Faculty of Physics, Adam Mickiewicz University*
Umultowska 85, 61-614 Poznań, Poland; e-mail: skumiel@amu.edu.pl

[(2)] *Institute of Natural Fibres and Medicinal Plants*
Wojska Polskiego 71b, 60-630 Poznań, Poland

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Ultrasonic emulsifying processes of immiscible liquids can be used to obtain stable emulsions. The authors used an ultrasonic sandwich head with an energy concentrator to obtain a suitable value of the energy density necessary for the emerge of ultrasonic cavitation. Two piezoelectric ring ($D_{\text{ext}} = 50$ mm) transducers of Pz-26 type produced by FERROPERM were used to design the ultrasonic sandwich head. The frequency of the ultrasonic wave was 18.4 kHz and the excitation time of the ultrasonic transducer exiting 5 minutes. Visible bubbles during the generation of ultrasonic waves appeared in the mixture after exceeding the cavitation threshold. The authors determined also the cavitation threshold by measuring the electrical voltage conducted to the transducers. To receive long-lasting emulsion, the electrical voltage attained 300 V_{peak}. The dispersion dependence on the emulsifying time was determined. The emulsion of linseed oil and water was stable through some months without surfactants.

Keywords: ultrasonic cavitation, ultrasonic emulsifying processes, emulsion, cavitation threshold.

1. Introduction

Emulsified vegetable oils are used as active ingredients (a.i.) of adjuvants increasing pesticides efficacy in agriculture. Such mixtures used as sprays for plants protection allow a better moistening of the surface of leaves and stems and thanks to that to improve the procedure efficiency and simultaneously to ensure their economical application.

The preparation of the emulsion is based on dispersion of one non-miscible liquid into the other one. In addition to the traditional mechanical method of preparation of oil and water emulsions, ultrasonic waves of lower frequency and large intensities ($\sim$10 W·cm^{-2}) can also be used for these purposes (Śliwiński, 2001; Jagodziński, 1997; Elpiner, 1968). Then, the emulgation processes are closely connected with ultrasonic cavitation. In the ultrasonic emulgation process, the dispersed-phase particles can achieve a large degree of size reduction (0.1÷0.5 μm) and the system shows an unquestionable homogeneity. Ultrasonic waves have a considerable influence on the coagulation and coalescence of emulgated particles. The oil-water emulsion is a dispersed system of two liquids: a polar and a nonpolar one and shows therefore a limited thermodynamic stability.

The use of an emulgator during emulgation increases the kinetic durability which is connected with the reduction of work required to prepare the emulsion (Elpiner, 1968; Lee, 1999). When the sonicated fluid contains additionally a gas phase in form of tiny (air or water stem) bubbles, it is easier to form an emulsion. Generally, the amount of the oil-water emulsion increases with the growth of the ultrasonic waves intensity. In turn, a considerable increase of temperature of the mixture during ultrasonic emulgation reduces the emulsion forming rate which is explained by the cavitation decrease. However, in the case of weak heating (30–40°C), the formation of the dispersed phase is slightly easier because of a viscosity and surface tension decrease of both components of the emulgating system. Moreover, the nature of the ultrasonic field has an influence on the intensification of the emulgation processes.

The coagulation of dispersed particles appears in the standing wave field. In aqueous systems, it pro-

ceeds in an antinode or in a node, depending on the density of the dispersed phase in comparison with that of the dispersed phase. If the density of the dispersion medium is higher than that of dispersed phase, the coagulation of disperse particles proceeds in the antinodes.

In the experiments carried out by the authors, a linseed oil and water were used in a wide range of concentrations. The linseed oil is produced by cold pressing of the *Linum usitatissimum* L. seeds cultivated in countries of dry, warm and moderate climate.

2. Experimental setup and methods

The measurement setup presented in Fig. 1 consists of a signal generator connected to a high frequency power amplifier model AL-300-HF-A ($P = 300$ W) which drives through a transformer two piezoceramic rings (Pz-26 type produced by Ferroperm). These rings are mechanically pressed with help of a steel bolt to back (steel) and front (aluminum) vibrating masses. Front acoustic mass vibrates with an aluminum concentrator of length corresponding to the half ultrasonic wave ($\lambda/2 \cong 125$ mm) (Gudra, 2000; Gudra, Ciszewski, 1979). The tip of the concentrator is immersed in the liquid medium ($V = 20$ ml), where a thermocouple temperature sensor of the thermoelectric thermometer is also placed. It makes possible the recording the temperature values during emulsification. During the propagation of the ultrasonic wave in a medium with an amplitude absorption coefficient α the release of the thermal energy – which volume density P_V is determined by the following expression (Nowicki, 1998):

$$P_V = I \cdot 2\alpha, \tag{1}$$

where I is the intensity of the ultrasounds – is occured. In the appendix, the authors presented a derivation of this formula.

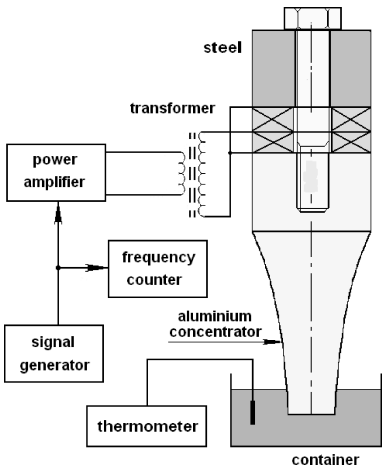

Fig. 1. Experimental setup for the investigation of the emulsifying processes in the mixture of linseed oil with water by the ultrasonic head of "sandwich" type with an acoustic wave concentrator.

The ultrasonic wave frequency at which the tip displacement has the maximum value was 18.4 kHz. The excitation time of the ultrasonic transducer was 5 minutes.

The linseed oil contained over 60% of linolenic acid (omega-3), 15% of linoleic acid (omega-6), 15% of oleic acid (omega-9) and a small amount of saturated fatty acids. The oil-water mixture poured into the container was 20 ml in volume.

3. Results

In the experiments, the authors used some values of concentration of the linseed oil in water (c_o = 5%, 30%, 50% and 70%). For each concentration, the time changes in temperature at selected values of the electric voltages over the cavitation threshold were recorded (Fig. 2).

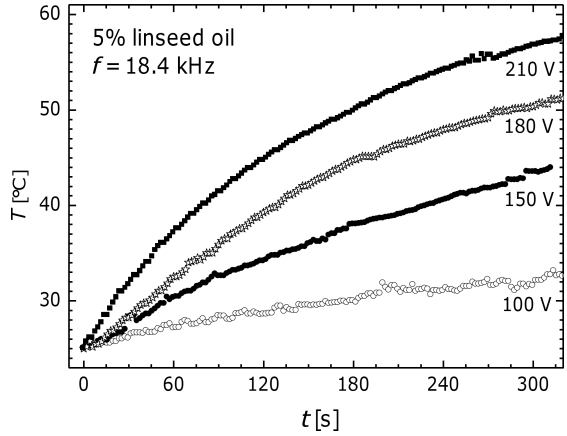

Fig. 2. Time changes in temperature in the container with a mixture of 5% linseed oil with water during the propagation of the ultrasonic wave for some selected voltage amplitudes fed to the piezoceramic rings.

All the records were taken with a start temperature of 25°C. Before switching on electrical voltage on the ultrasonic transducers, two liquids were mixed up and each phase looked transparent. An non-transparent white emulsion was created in the container when the electrical voltage was switched on. The increase in the temperature was the result of heat energy losses caused by the propagation of a high intensity ultrasonic wave in the real dissipative medium.

4. Discussion

There is a determined limit of the emulsion concentration increase, which can be explained by a state of equilibrium of formation between two opposite processes, which take place between the emulgation and coagulation. The defined emulsion concentration corresponds to a given ultrasonic wave intensity. The time changes in temperature presented in Fig. 2 have differ-

ent values of the temperature slope at the initial time ($t \geq 0$). Taking into account the experimental values of $(\mathrm{d}T/\mathrm{d}t)_{t\geq 0}$ for different voltages, we obtained for example dependences shown in Figs. 3. A very good agreement between the experimental data and the fitted funcation was obtained using the following expression:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t=0} = a \cdot \left(\frac{U}{U_0}\right)^n, \tag{2}$$

where a, U_0 and n are parameter values from the fit procedure. In Table 1, the a, n and U_0 parameter values from the fit procedure are listed.

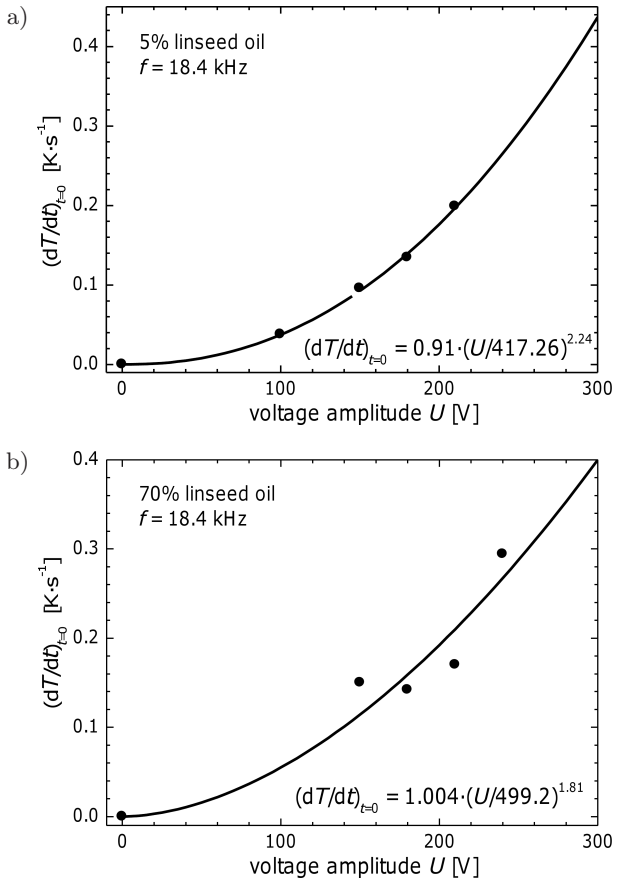

Fig. 3. The temperature rate $(\mathrm{d}T/\mathrm{d}t)_{t=0}$ during propagation of the ultrasonic wave in the sample in the initial period since switching on the electrical voltage U for two concentrations of linseed oil in water: a) 5%, b) 70%.

Table 1. Parameter values of a, U_0 and n obtained from the fitting of function (2) to the experimental data of the temperature increase rate $(\mathrm{d}T/\mathrm{d}t)_{t=0}$.

Concentration of linseed oil in water c_o [%]	a [K·s^{-1}]	U_0 [V]	n [–]
5	0.9139	417.3	2.238
30	1.018	486.1	1.639
50	1.087	465.3	1.918
70	1.004	499.2	1.806

According to calorimetric law, the heat losses power of density released in the sample is equal to:

$$P_v = \rho_{\mathrm{em}} \cdot C_{\mathrm{Pem}} \cdot \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t=0} \left[\frac{\mathrm{W}}{\mathrm{cm}^3}\right], \tag{3}$$

where ρ_{em} [g·cm^{-3}] is the emulsion density and C_{Pem} [J·g·K^{-1}] is the specific heat capacity of the emulsion. Taking into account Eq. (3), we made the graphic presentation of the heat power density as shown in Fig. 4. The solid lines are functions which were made with the help of Eqs. (2) and (3).

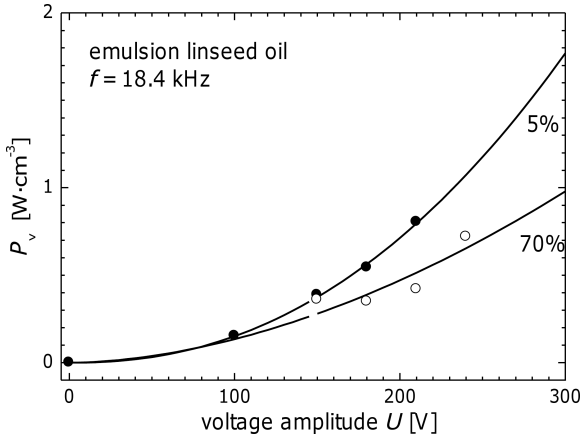

Fig. 4. The dependencies between the heat losses power density released in the sample during propagation of the ultrasonic wave and the electrical voltage amplitude (fed to piezoceramic rings) for two selected concentrations of linseed oil in water.

In turn, Fig. 5 presents the dependence of the heat losses power density P_V and the linseed oil concentration c_o in water for selected electrical voltage amplitudes ($U = 300\ \mathrm{V}_p$). In this case the authors applied

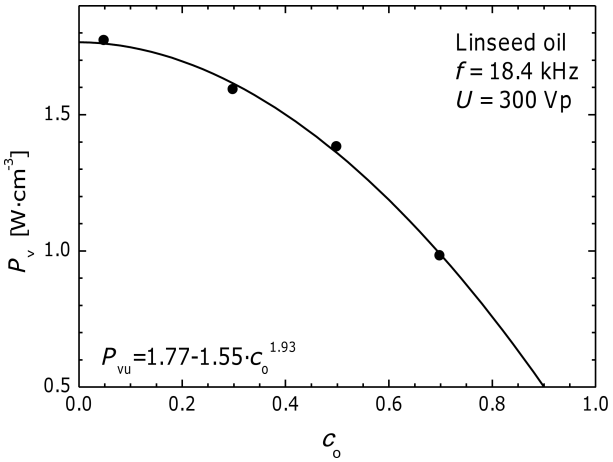

Fig. 5. The dependence of the heat losses power density released in the sample during the propagation of ultrasonic wave on the concentration of linseed oil in water for a selected electrical voltage amplitude.

Table 2. Values of heat losses power density P_V, absorption of ultrasonic wave coefficient α and ultrasonic wave intensity I for some concentrations of linseed oil in water.

Concentration of linseed oil in water c_o	ρ_{em} (Niesteruk, 1996)	C_{Pem} (Niesteruk, 1996)	P_V at $U = 300$ V	α at 18.4 kHz	$I = P_V/(2 \cdot \alpha)$ at 18.4 kHz
%	g·cm^{-3}	J·g^{-1}·K^{-1}	W·cm^{-3}	cm^{-1}	W·cm^{-2}
5	0.997	4.071	1.77	0.0164	54.02
30	0.979	3.513	1.59	0.0911	8.73
50	0.966	3.052	1.38	0.1341	5.14
70	0.952	2.578	0.98	0.1622	3.02

the following expression as the fitting function to experimental data:

$$P_v = b - k \cdot c_o^N \quad \left[\frac{\text{W}}{\text{cm}^3}\right], \tag{4}$$

where b, k and N are parameters obtained from the fitting procedure. For the electrical voltage amplitude $U = 300\,\text{V}_p$, the values of those parameters are: $b = 1.766$, $k = 1.55$ and $N = 1.927$.

Table 2 contains values of the heat losses power density P_V, the absorption of ultrasonic wave coefficient α and the ultrasonic wave intensity I for some concentrations of linseed oil in water. In the literature (Basaran *et al.*, 1998), we found for oil-in-water emulsions the absorption coefficient values measured at frequency $f_1 = 5$ MHz. Because our experiments were carried out at a considerably smaller frequency ($f = 18.4$ kHz), we can use the following equation (Nowicki, 1998; Jaroszyk, 1993):

$$\alpha = \alpha_1 \left(\frac{f}{f_1}\right)^p, \tag{5}$$

where $p \cong 2$.

5. Conclusions

The decreasing of the ultrasonic wave amplitude propagating through the emulsion is caused by absorption, scattering and divergence of the ultrasounds. To exceed a cavitation threshold, a voltage amplitude over 100 V on the converters is required.

The emulgation process is accompanied by a heat released in the emulgated medium.

The oil-water emulsions are much more stable than water-oil emulsions obtained without any emulgator.

Appendix. Derivation of the dependence of the heat losses power density on the ultrasonic wave intensity

Imagine that a flat ultrasonic wave propagates in a liquid lossy medium.

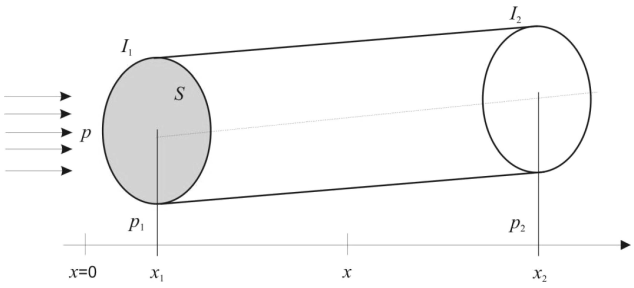

Fig. 6. Ultrasonic wave in a lossy medium.

In position x_1 the pressure amplitude is p_1, and in position x_2 it is p_2

$$p(x) = p_1 \cdot e^{-\alpha(x-x_1)}, \quad p_2 = p_1 \cdot e^{-\alpha(x_2-x_1)}, \tag{6}$$

where α is the amplitude absorption coefficient of this medium, $x_2 - x_1 = l$.

Since the amplitude of the ultrasonic wave intensity is proportional to the second power of the amplitude ultrasonic pressure

$$I \propto p^2, \tag{7}$$

we can write:

$$I(x) = I_1 \cdot e^{-2\alpha(x-x_1)}, \quad I_2 = I_1 \cdot e^{-2\alpha(x_2-x_1)}. \tag{8}$$

There is a following difference between I_1 and I_2:

$$\Delta I = I_2 - I_1 = I_1 \cdot e^{-2\alpha(x_2-x_1)} - I_1 \tag{9}$$

$$= I_1 \cdot \left(1 - e^{-2\alpha \cdot l}\right). \tag{10}$$

Taking into account that the difference in the ultrasonic wave intensities ΔI on the length l is caused by the heat power losses P, we can write:

$$P = I_1 \cdot \left(1 - e^{-2\alpha \cdot l}\right) \cdot S, \tag{11}$$

where S is the cross-section of ultrasonic wave beam.

The volume between the points $x_2 - x_1$ is $V = S \cdot l$, thus the heat losses power density P^* is equal:

$$P^* = \frac{P}{V} = \frac{I_1 \cdot \left(1 - e^{-2\alpha \cdot l}\right) \cdot S}{l \cdot S} = \frac{I_1}{l} \cdot \left(1 - e^{-2\alpha \cdot l}\right). \tag{12}$$

Replacing $e^{-2\alpha l} \cong 1 - 2\alpha l$, we obtained finally:

$$P^* = \frac{I_1}{l} \cdot (1 - 1 + 2\alpha \cdot l) = 2 \cdot \alpha \cdot I_1 \quad \left[\frac{\mathrm{W}}{\mathrm{m}^3}\right], \quad (13)$$

where P^* is the heat losses power density and I_1 is the ultrasonic wave intensity.

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