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 ($D_{ext} = 50$ 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
cogulation of disperse particles proceeds in the anti-
odes.

In the experiments carried out by the authors, a lin-
seed oil and water were used in a wide range of concen-
trations. The linseed oil is produced by cold pressing of
the *Linum usitatissimum* L. seeds cultivated in coun-
tries 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 con-
centrator of length corresponding to the half ultra-
sonic wave (∆/2 ≈ 125 mm) (GUDRA, 2000; GUDRA,
CISZEWSKI, 1979). The tip of the concentrator is im-
nersed in the liquid medium (*V* = 20 ml), where a
thermocouple temperature sensor of the thermoelec-
tric thermometer is also placed. It makes possible the
recording the temperature values during emulsifica-
tion. During the propagation of the ultrasonic wave
in a medium with an amplitude absorption coefficient
*a* the release of the thermal energy – which volume
density *P*<sub>V</sub> is determined by the following expression
(NOWICKI, 1998):

\[ P_V = I \cdot 2 \alpha, \]  

(1)

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

The ultrasonic wave frequency at which the tip dis-
placement has the maximum value was 18.4 kHz. The
excitation time of the ultrasonic transducer was 5 min-
utes.

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 val-
ues of concentration of the linseed oil in water (*c*<sub>0</sub> =
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).

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 con-
centration increase, which can be explained by a state
of equilibrium of formation between two opposite pro-
cesses, which take place between the emulgation and
coagulation. The defined emulsion concentration cor-
responds to a given ultrasonic wave intensity. The time
changes in temperature presented in Fig. 2 have differ-

![Fig. 1. Experimental setup for the investigation of the emul-
sifying processes in the mixture of linseed oil with water by
the ultrasonic head of “sandwich” type with an acoustic
wave concentrator.](image)

![Fig. 2. Time changes in temperature in the container with
a mixture of 5% linseed oil with water during the prop-
agation of the ultrasonic wave for some selected voltage
amplitudes fed to the piezoceramic rings.](image)
ent values of the temperature slope at the initial time \( t \geq 0 \). Taking into account the experimental values of \( \frac{dT}{dt} \rangle \geq 0 \) for different voltages, we obtained for example dependences shown in Figs. 3. A very good agreement between the experimental data and the fitted function was obtained using the following expression:

\[
\left( \frac{dT}{dt} \right)_{t=0} = a \cdot \left( \frac{U}{U_0} \right)^n,
\]

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.

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

\[
P_v = \rho_{\text{em}} \cdot C_{\text{Pem}} \cdot \left( \frac{dT}{dt} \right)_{t=0} \left[ \frac{W}{\text{cm}^3} \right],
\]

where \( \rho_{\text{em}} \) [g·cm\(^{-3}\)] is the emulsion density and \( C_{\text{Pem}} \) [J·g\(^{-1}\)·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. 3. The temperature rate \( \left( \frac{dT}{dt} \right)_{t=0} \) 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 \( \left( \frac{dT}{dt} \right)_{t=0} \).

<table>
<thead>
<tr>
<th>Concentration of linseed oil in water ( c_o ) [%]</th>
<th>( a ) [K·s(^{-1})]</th>
<th>( U_0 ) [V]</th>
<th>( n ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.9139</td>
<td>417.3</td>
<td>2.238</td>
</tr>
<tr>
<td>30</td>
<td>1.018</td>
<td>486.1</td>
<td>1.639</td>
</tr>
<tr>
<td>50</td>
<td>1.087</td>
<td>465.3</td>
<td>1.918</td>
</tr>
<tr>
<td>70</td>
<td>1.004</td>
<td>499.2</td>
<td>1.806</td>
</tr>
</tbody>
</table>

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 \( U = 300 \text{ V}_p \). In this case the authors applied

Fig. 5. The dependence of the heat losses power density \( P_v \) released in the sample during the propagation of ultrasonic wave on the concentration of linseed oil in water for a selected electrical voltage amplitude.
the following expression as the fitting function to experimental data:

$$P_{V} = b - k \cdot e^{N} \left[ \frac{W}{cm^{3}} \right], \quad (4)$$

where $b$, $k$ and $N$ are parameters obtained from the fitting procedure. For the electrical voltage amplitude $U = 300$ V, 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 $\alpha$ and 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):

$$\alpha = \alpha_1 \left( \frac{I}{I_1} \right)^{p}, \quad (5)$$

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.

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

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

where $\alpha$ 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

$$I \propto p^2, \quad (7)$$

we can write:

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

There is a following difference between $I_1$ and $I_2$:

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

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

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

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

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:

$$P^* = \frac{P}{V} = \frac{I_1 \cdot (1 - e^{-2\alpha l}) \cdot S}{l \cdot S} = \frac{I_1}{l} \cdot (1 - e^{-2\alpha l}). \quad (12)$$
Replacing $e^{-2\alpha l} \simeq 1 - 2\alpha l$, we obtained finally:

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

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

**References**