Destruction of Oil-Water Emulsions in an Ultrasonic Field

G I Volkova\textsuperscript{1,2} and N V Yudina\textsuperscript{2}
\textsuperscript{1}Tomsk State University, 36, Lenin Avenue, Tomsk, 634050, Russia
\textsuperscript{2}Institute of Petroleum Chemistry Russian Academy of Sciences, Siberian Branch, 4, Akademichesky Avenue, Tomsk, 634055, Russia

galivvol@yandex.ru

Abstract. Effect of impact of acoustic conditions on the breakdown of a stable oil-water emulsion is studied. The emulsion contains 80, 10 and 10 wt% of a solution of petroleum paraffin in 6 wt% of kerosene, distilled water, and highly resinous oil, respectively. Samples are treated in an ultrasonic field for 1-15 min at a frequency of 22 kHz, intensities 2, 6, 18 W/cm\textsuperscript{2}, and temperatures 0 and 20 °C. It is shown that under optimal conditions of treatment (temperature 20 °C, 10 min, field intensity 18 W/cm\textsuperscript{2}) ultrasound causes the breakdown of the model emulsion. After demulsification, water, paraffins, and asphaltenes are concentrated in the lower layer. Ultrasonic treatment can be successfully used to treat watercut oils for transport.

1. Introduction

Currently, oil demulsification is performed by such methods as centrifugation [1], microwave radiation [2], microwave electromagnetic radiation [3], and low-frequency acoustic treatment [4]. These methods are quite effective for dehydration of light crude oil but chemical demulsifiers are additionally used almost always and especially for heavy crude oil.

The ultrasound is widely used in the processes of demulsification of crude oil. The use of ultrasound for the breaking of emulsions with various physicochemical properties is also of great interest for researchers. According to Gardner E.A. and Apfel R.E. [5], cavitation can strongly affect systems with immiscible liquids. In the case of using a powerful ultrasonic device, cavitation can break the drops into smaller droplets by destroying their surface layer. As a result, stable emulsions can be formed. On the other hand, droplets may merge under the action of cavitation, which will lead to the release of water from oil. Stimulation of the breakdown of the emulsion by cavitation is possible if the injected energy is sufficient to destroy the protective shell of the droplets but not to disperse the particles.

In [6], the effect of several ultrasonic frequencies on the stability of a heavy oil emulsion was evaluated. The use of ultrasonic treatment for 15 min at the frequencies 25, 35, and 45 kHz allowed the emulsion of crude oil to be broken with an efficiency of up to 60 %. Based on the investigations, it was concluded that in order to achieve maximum demulsification efficiency, it is necessary to vary the time of treatment in accordance with the composition of the emulsion. In author’s opinion, the effect may be due to the turbulence in the emulsion caused by cavitation or the flow of sound energy.

This work deals with the study of the effect of time, temperature, and intensity of ultrasonic treatment on the stability of a model emulsion containing 80, 10, and 10 wt% of a solution of petroleum paraffin in 6 wt% of kerosene, distilled water, and highly resinous oil, respectively.
2. Experimental methods and materials

The object of the study was a model emulsion, where the dispersed phase was formed using distilled water and 6 wt% of a solution of petroleum paraffin in kerosene (PP-k). The composition of the dispersion medium was changed by adding highly resin low-paraffin oil to the organic phase. This oil contained 59 wt% of oils (including 1 wt% of paraffinic hydrocarbons), 31.1 wt% of resins, and 9.9 wt% of asphaltenes. Model emulsions were prepared using a mechanical stirrer at a shaft rotation speed of 3000 rpm for 10 min at room temperature. Emulsions were treated at the field frequency 22 kHz and the field intensities (I) of 2, 6 and 18 W/cm². Samples were ultrasonically treated, hence thermostated at 0 or 20 °C within 1-15 minutes. The resistance of emulsion to ultrasound was estimated using the “bottle test” method and by the water content in the oil layer in accordance with the GOST 2477-65. The microstructure of the emulsions was analyzed using an AXIO LAB.A1 Carl Zeiss optical microscope. IR spectra were recorded using a NICOLET 5700 FTIR spectrometer in the range 400-4000 cm⁻¹. The processing of the spectra and determination of the optical density were performed using OMNIC 7.2 Thermo Nicolet Corporation software.

3. Results and Discussion

Emulsions containing 80, 10, 10 wt% of a solution of PP-k, distilled water and oil, respectively, were stable [7]. According to the data of optical microscopy, the initial emulsion was represented by spherical particles 1-17 μm in size, and the maximum distribution was 4 μm (Figures 1, 2a). If an ultrasonic treatment (UT) was carried out at a bath temperature of 20 °C and a field intensity of 2 W/cm² for 1 min, the emulsion remained stable during the treatment, but the pattern of the particle size distribution changed.

According to microscopy data, two processes occurred simultaneously in the emulsion after UT: aggregation of small particles and dispersion of the large ones. The maximum of particle size distribution shifted to the region of 7.5 μm (Figure 1). An increase in the time of treatment to 15 min led to the appearance of large particles up to 50 μm, which were held by air bubbles with a size of about 1 μm (Figure 2b). The treatment of the emulsion at the bath temperature 0 °C at the same field intensity and the time of treatment promoted breakdown of the sample. The upper layer contained small droplets of water and translucent aggregates (Figure 3a), while the lower one was a multiple emulsion: large droplets of water in the organic phase, in which micron particles of water were embedded (Figure 3b).

![Figure 1. Water droplet size distribution in the emulsion.](image-url)
Figure 2. Microphotographs of the emulsion: a – initial emulsion, b – emulsion after 15 minutes of UT at $I = 2 \text{ W/cm}^2$ and bath temperature 20 °C.

Figure 3. Microphotographs of the emulsion: a – the upper layer, b – the lower layer; after 15 min of UT, $I = 2 \text{ W/cm}^2$, bath temperature 0 °C.

Figure 4. Micrograph of the emulsion after UT for 1 min at an intensity of 18 W/cm² and bath temperature 20 °C.

Exposure of the sample to the field of intensity 18 W/cm² for 1 min at room temperature has resulted in a change in the shape and size of water droplets. Droplets merged to form ellipsoidal aggregates up to 50 μm in size (Figure 4). A longer treatment (5-15 min) caused the release of a solid phase (Figure 5a), large particles of which were sedimented together with large particles of water one hour after (Figure 5b). The micrograph of the lower layer is similar to the image shown in Figure 3b.

The upper and lower layers of the treated emulsion are separated after 1 hour of holding. The upper layer contained 0.41, 0.35 and 0.27 wt% of water after 1 min of treatment at a field intensity of 2, 6, and 18 W/cm², respectively (Table 1). There was no water in the upper layer after a longer treatment of the emulsion at a field intensity of 2 and 6 W/cm².
Figure 5. Microphotographs of the emulsion: a – the upper layer, b – the lower layer one hour after 15 min of UT; $I = 18$ W/cm$^2$, bath temperature 20 °C.

Table 1. Effect of UT conditions on the stability of the emulsion and the water content in the upper layer.

| Field intensity [W/cm$^2$] | Time [min] | Stability                      | Water content [wt%] (one hour after UT) |
|-----------------------------|------------|--------------------------------|----------------------------------------|
| Without UT                  | -          | undemulsified                  | 10                                     |
| 2                           | 1          | demulsified 1 hour after the ultrasonic treatment | 0.41                                   |
|                             | 5          | demulsified immediately after the ultrasonic treatment | none                                   |
|                             | 10         | demulsified immediately after the ultrasonic treatment | none                                   |
| 6                           | 1          | demulsified 1 hour after the ultrasonic treatment | 0.35                                   |
|                             | 5          | demulsified immediately after the ultrasonic treatment | none                                   |
|                             | 10         | demulsified immediately after the ultrasonic treatment | none                                   |
|                             | 15         | demulsified immediately after the ultrasonic treatment | none                                   |
| 18                          | 1          | demulsified 1 hour after the ultrasonic treatment | 0.27                                   |
|                             | 5          | demulsified immediately after the ultrasonic treatment | none                                   |
|                             | 10         | demulsified immediately after the ultrasonic treatment | none                                   |
|                             | 15         | demulsified immediately after the ultrasonic treatment | none                                   |

The lower layer was dehydrated and investigated using the methods of IR spectroscopy and column adsorption chromatography. The dehydrated lower layer was partially fractionated with hexane.

According to the data of IR spectroscopy, the ratio of spectral coefficients is the same in two samples – asphaltenes isolated from the used oil and in the hexane insoluble fraction isolated from the lower layer (Figure 6). Hence, it can be stated with a high degree of reliability, that after UT the asphaltenes of the introduced oil are aggregated and sedimented in the water layer. As for the deasphalting agent (eluent) of the lower layer, it is substantially enriched with paraffins in comparison with the initial emulsion. The values of spectral coefficients ($D_{290}/D_{1465}$) evaluating the conditional content of paraffin structures are 0.275 and 0.165 rel. units for deasphaltizate and PP-k solution, respectively.
Figure 6. Spectral coefficients of oil asphaltenes and sediment insoluble in hexane.

A comparison was made of the component composition of the initial mixture and the dehydrated organic part of the lower layer after demulsification. The content of the components in the initial mixture was calculated based on the composition of the emulsion. The group composition of the organic part of the lower layer was determined by column adsorption chromatography. The initial sample contains 53.5, 5.3 and 16.7 wt% of PP, asphaltenes and resins, respectively (Figure 7a). After UT and demulsification in the lower layer, the content of asphaltenes increases by 62% and that of paraffin hydrocarbons by 47%. This is consistent with the data of IR spectroscopy (Figure 7b).

Figure 7. Content of components (wt%) in the initial emulsion (a) and in the lower layer after demulsification (b).

Conclusions
Thus, low-frequency ultrasound (22 kHz) causes demulsification of stable emulsions at optimal parameters of ultrasonic treatment: temperature 20 °C, time 5-15 min, field intensity 18 W/cm². After UT of model emulsions during 5-15 minutes water was absent in the upper layer of the system, while in the lower layer the concentrations of water, asphaltenes and paraffins have been observed. Ultrasound can be used not only for the treatment of oil-water emulsions before transport but also for their deasphaltization.

Acknowledgments
This work was supported by the Ministry of Science and High Education of the Russian Federation (Project No 44.3.1).
References

[1] Hahn A U and Mittel K L 1979 Mechanism of demulsification of oil-in-water emulsion in the centrifuge Colloid. Polym. Sci. 257 pp 959-967

[2] Diehl L O et al 2011 Separation of Heavy Crude Oil Emulsions Using Microwave Radiation for Further Crude Oil Analysis Sep. Sci. Technol. 46 pp 1358-1364

[3] Kovaleva L A et al 2017 Study of integrated effects microwave electromagnetic radiation in the field of centrifugal forces on the water-oil emulsion Oil Industry no. 2 pp 100-103

[4] Mordvinova Yu N and Loskutova Yu V 2019 The influence of low-frequency acoustic exposure on the stability of oil-water emulsions Proceedings of the XXIII International Acad. M.A. Usov Symposium for students and young scientists dedicated to the 120th anniversary of Acad. K.I. Satpayev and 120th anniversary of Prof. K.V. Radugin, Tomsk, April 8-12, 2 TPU Publishing House pp 344-346

[5] Gardner E A and Apfel R E J 1993 Using acoustics to study and stimulate the coalescence of oil drops surrounded by water Colloid Interface Sci. 159 pp 226-237

[6] Antes F G et al 2017 Feasibility of low frequency ultrasound for water removal from crude oil emulsions Ultrason. Sonochem. 35 pp 541-546

[7] Volkova G I and Yudina N V 2018 Effect of resin-asphaltene substances on the stability of inverted emulsions AIP Conference Proceeding 2051 pp 020323 https://doi.org/10.1063/1.5083566