Influence of ultrasonic treatment on kinetic of asphaltene aggregation in toluene/heptane mixture

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Abstract. This article illustrates the results of a study of ultrasonic dispersion’s influence on kinetic of asphaltene aggregation in a toluene/heptane mixture. The study was carried out by the method of dynamic light scattering. This optical method allows to measure the size of nano- and submicron particles in liquid medium. This method allows to measure the dependence of the average size of asphaltene aggregates during primary and secondary asphaltene aggregation. The primary aggregation was studied in a solution of asphaltenes in toluene and was initiated by the addition of heptane. Secondary aggregation of asphaltenes was initiated by ultrasonic dispersion of a mixture of toluene/heptane/asphaltene, in which primary aggregation finished and which contained asphaltene flocules. The effect of stabilization of asphaltene aggregates was experimentally detected after multiple ultrasonic dispersions.

1. Introduction

Phase transitions in natural hydrocarbon systems vastly determine the physical phenomena inherent in the processes of development and exploration of oil and gas fields. Knowledge of phase transformations pattern and the ability to predict them allows to develop methods for enhancing oil and gas condensate recovery, to design effective technological schemes for processing and transporting extracted raw materials. Due to the growth of heavy oil production, interest in the study of the physicochemical properties of asphaltenes increases every year. An important research issue is to understand the reasons for the loss of stability of oil in relation to the precipitation of heavy fractions. Heavy oil fractions are mainly resins, asphaltenes and paraffins. The formation of asphalt-resin-paraffin deposits significantly complicates the technological processes of oil production, transportation and processing. Both mechanical and physicochemical methods are exploited to combat such deposits.

Methods using ultrasonic treatment are prospective tools for combating asphalt-resin-paraffin deposits. Studies of ultrasound effect on the reservoir and oil fluids have been conducted for a long time. Nowadays it still arises the interest of many researchers around the world. The works [1-5] are devoted to the study of the ultrasonic influence on oil, its properties and directly on asphaltenes. The studies [6-8] help to understand the influence of ultrasonic waves on the near well area for the intensification of oil production. The studies [9-12] describes the influence of ultrasonic treatment for upgradation of the petroleum residue to valuable product and intensify the cracking of asphaltene present in the vacuum residual feedstock.

It is necessary to note, that in spite of the large number of studies showing various positive effects of ultrasonic oil treatment, the mechanism of ultrasonic effect on the aggregation of asphaltenes at the...
submicron level is not well studied. This kind of research is convenient to conduct on model systems (solvent/precipitator/asphaltenes), which will avoid the influence of other oil components on the results of the study. As it was shown earlier in [13], if a sample of an asphaltene solution in which the aggregation process takes place is subjected to mixing or ultrasonic dispersion, then it is possible to destroy the asphaltene aggregates formed by this time to the size from which the growth of these aggregates began. At the same time, the destroyed aggregates tend to re-associate. However, the discovered effect was not explicitly explored in this work. In publications, it was not possible to find references to the study of this effect, which can be called repeated (secondary) aggregation or re-aggregation of asphaltene aggregates/flocules. Also, the effect of ultrasonic treatment on the aggregation of asphaltenes in model systems (toluene/heptane or toluene/pentane) was studied in [15, 16].

In this work, the kinetics of asphaltenes aggregation from a solution in toluene after the addition of heptane and the effect of ultrasound on the asphaltene aggregates formed after this aggregation are studied by the DLS method.

2. Materials and Methods
Dynamic Light Scattering (DLS) is an experimental method for measuring the size of nanoparticles in a liquid medium. This method is applicable for particles ranging in size from 0.5 nm to several micrometers and is based on the measurement of the correlation function of fluctuations in the intensity of scattered light. The method of dynamic light scattering allows to study the effect of ultrasonic treatment on the formation of supramolecular structures in oil systems at the submicron and nanoscale.

In this study, the dynamic light scattering measurements were performed on the Photocor Complex equipment (Photocor, Russia). This device used a He-Ne laser with a wavelength of 632 nm and a power of 15 mW. To reduce the effect of heating the sample by laser radiation, the laser power has been reduced by a neutral filter by 30 times. The scattering angle in all measurements was 50 degrees. The measurement time of each correlation function was 60 seconds. All measurements were carried out at room temperature (25°C).

A.E. Arbuzov Institute of Organic and Physical Chemistry provided samples of asphaltenes. Asphaltenes were obtained from the Romashkinskaya crude oil (Tatarstan, Russia) by adding forty times the volume of petroleum ether to the oil volume. The resulting solid phase was filtered out and washed with heptane to wash off the remaining resins and dried after all. Toluene and heptane (reagent grade) were purchased from Ecos-1, Russia. The components were weighed during the preparation of the mixtures on a Sartorius BP301S scale with a resolution 0.1 mg (Germany).

Hermetically sealed glass vials with the studied samples were dispersed on an ultrasonic disperser UZDN-A (300 W, 22 kHz, Russia). This device has a mode of operation that allows one to perform ultrasonic treatment by placing the vial in a small titanium glass of water with a volume of about 100 ml. Through the walls of this glass, an ultrasound effect was transmitted to the water. Ultrasonic waves affected the walls of the vial and the sample in it through the water. Thus, there were conditions similar with the operating conditions of the ultrasonic bath.

At first, a solution of asphaltenes in toluene 0.1 g/L was prepared. It was kept in a dark place at room temperature for more than a day after preparation to completely dissolve the asphaltenes and reach an equilibrium. In this sample, heptane was added in such an amount that 69% of the weight of heptane was obtained in the final mixture. Measurements were made on this sample during the course of primary aggregation. The heptane concentration of 69% by weight was appropriate because it is obviously higher than the threshold concentration of the beginning of aggregation in this sample, which is about 50% by weight and at the same time not too high, which allows to observe the growth of asphaltene aggregates by DLS for a long time (tens and hundreds of minutes). At least 10 hours after the addition of heptane, when the asphaltene aggregation process in the sample was measured by DLS and finished and sediment formed on the bottom, the sample was subjected to ultrasonic treatment for 30 seconds. Right after that, the process of measuring the particle size in such a sample
using the DLS method was started again. This process of dispersing and measuring the sample was repeated 6 times, with an interval between dispersions of at least 10 hours required to complete aggregation in the sample.

3. Results and discussion

The aggregation of asphaltenes that proceeds after the addition of the precipitator to the solution of asphaltenes in toluene will be called primary. The aggregation of asphaltenes that fell out of the solution earlier and were subjected to mechanical or cavitation action for crushing into smaller parts will be called secondary aggregation. Herewith, on one sample of solvent-asphaltenes-precipitator secondary aggregation can be initiated repeatedly. In this case, we can talk about the number of cycles of secondary aggregation on this sample. One cycle of secondary aggregation consists of the process of breaking the asphaltene aggregates present in the sample into smaller ones by mechanical mixing of the sample, or ultrasonic dispersion and the process of aggregation of the structures formed after such exposure. Figure 1 shows the dependences of the average hydrodynamic radius of asphaltene aggregates measured during the primary aggregation and during the first cycle of secondary aggregation by means of DLS. It is clear, that the time dependence of the average size of asphaltene aggregates during the primary aggregation and the first cycle of secondary aggregation are similar. In the first minutes of measurement, right after the addition of heptane (primary aggregation) or dispersion (secondary aggregation), the radius of asphaltene particles in the sample is about 100 nm. In approximately 40 minutes, the average size of asphaltene particles reaches a size of about 0.5 micrometer. Over time asphaltene aggregates become so large that they can no longer remain suspended in the volume of the sample and settle to the bottom of the vial. It was shown in [13, 14] that the aggregation of asphaltenes has a diffusion-limited character.

![Figure 1](image.png)

**Figure 1.** Hydrodynamic radius of asphaltene aggregates versus time. Sample 0.1 g/L of asphaltene in toluene with 69 mass% heptane addition. Primary aggregation (red circles) and secondary aggregation (blue squares) on the same sample after sonication.

Figure 2 demonstrates the dependences of the average hydrodynamic radius of asphaltene particles in the sample during primary aggregation and during several cycles of secondary aggregation. Figure 2 clearly illustrates that the dependences of the average particle size on time during primary aggregation and after the first three cycles of secondary aggregation are similar. However, already at the fourth cycle of secondary aggregation, a significant slowdown in the growth of asphaltene particles in the
sample is evident. At the sixth cycle of secondary aggregation, the growth of asphaltene particles seems to stop. Hence, repeated dispersion led to the appearance of stable particles in the sample with a size (radius) of about 200 nm.

![Graph](image)

**Figure 2.** Hydrodynamic radius of asphaltene aggregates versus time for multiple ultrasonic dispersion. Sample 0.1 g/L of asphaltenes in toluene with 69 mass% heptane addition.

Presumably, the asphaltene molecules in the process of flocculation after the addition of heptane to the solution of asphaltenes in toluene above the threshold concentration can stick together strongly enough as well as weakly. This leads to the fact that the emerging asphaltene flakes are quite fragile and can be destroyed by simple mechanical mixing or shaking. As a matter of fact, the flakes will obviously be destroyed in places where the asphaltenes have stuck together weakly. At the same time, the particles of these broken flakes again tend to couple and again can stick together both strongly enough and weakly, as it was before. Such periodic destruction of flakes in places of weak connection of asphaltene molecules and their subsequent adhesion can lead to the appearance of particles with a mainly strong type of connection of asphaltene molecules in them. Such particles, apparently, are already significantly less likely to aggregate with each other and can remain suspended in the sample volume for a long time. It is important to note that we know of asphaltene samples for which the appearance of stable particles with a size of about 200 nm was observed after a larger number of secondary aggregation cycles. There were also samples in which, after 20 cycles of secondary aggregation, stabilized particles did not appear. The observed in this work effect is possibly related to the chemical composition of the asphaltene sample and this is the goal of further research.

It is interesting fact that with the help of ultrasonic dispersion, stable emulsions of n-alkanes, their mixtures, petroleum paraffins, oils and bitumens can be obtained in water without the addition of surfactants [17-20]. The droplet size in such emulsions is approximately 100-200 nm, and the zeta-potential is up to -50 mV. Such a high zeta-potential in such systems can remain in a quite wide pH range of the medium [21].

4. Conclusions
This study demonstrates that the dependences of the average particle size on time in toluene/asphaltene/heptane solution during primary aggregation and during the first cycle of secondary aggregation are similar. After several cycles of destruction by ultrasonic dispersion and subsequent
growth of asphaltene particles, stable particles with a size (radius) of about 200 nm can be formed in such a sample. The results of these researches will be useful for understanding the mechanism of the effect of ultrasonic treatment on asphaltene aggregates and the development of methods using ultrasound to improve the efficiency of oil production, transportation and oil refining.

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5. References
[1] Liu J, Yang F, Xia J, Wu F and Pu C 2021 Mechanism of ultrasonic physical–chemical viscosity reduction for different heavy oils ACS Omega 6 2276–83
[2] Shedid S A and Attallah S R 2004 Influences of ultrasonic radiation on asphaltene behavior with and without solvent effects SPE International Symposium and Exhibition on Formation Damage Control (Society of Petroleum Engineers)
[3] Salehzadeh M, Akherati A, Ameli F and Dabir B 2016 Experimental study of ultrasonic radiation on growth kinetic of asphaltene aggregation and deposition Can. J. Chem. Eng. 94 2202–9
[4] Najafi I and Amani M 2011 Asphaltene flocculation inhibition with ultrasonic wave radiation: a detailed experimental study of the governing mechanisms Adv. in Petroleum Exploration and Development 2 32-36
[5] Simkin E M 1993 A possible mechanism of vibroseismic action on an oil-bearing bed J. Eng. Phys. Thermophys. 64 355–9
[6] Ghazanfari M H, Keshavarzi B and Ghotbi C 2018 Application of ultrasonic wave for stimulation of asphaltene damaged reservoir rocks: an experimental study Sci. Iran. 0–0
[7] Wong S-W, van der Bas F, Groenboom J and Zuiderwijk P 2003 Near wellbore stimulation by acoustic waves SPE European Formation Damage Conference (Society of Petroleum Engineers)
[8] Champion B, van der Bas F and Nitters G 2004 The application of high-power sound waves for wellbore cleaning SPE Prod. Facil. 19 113–21
[9] Gopinath R, Dalai A K and Adjaye J 2006 Effects of ultrasound treatment on the upgradation of heavy gas oil Energy & Fuels 20 271–7
[10] Mohapatra D P and Kirpalani D M 2016 Bitumen heavy oil upgrading by cavitation processing: effect on asphaltene separation, rheology, and metal content Appl. Petrochemical Res. 6 107–15
[11] Kaushik P, Kumar A, Bhaskar T, Sharma Y K, Tandon D and Goyal H B 2012 Ultrasound cavitation technique for up-gradation of vacuum residue Fuel Process. Technol. 93 73–7
[12] Kang N, Hua I and Xiao C 2006 Impacts of sonochemical process variables on number average molecular weight reduction of asphaltene Ind. Eng. Chem. Res. 45 5239–45
[13] Yudin I K and Anisimov M A Dynamic light scattering monitoring of asphaltene aggregation in crude oils and hydrocarbon solutions asphaltenes, Heavy Oils, and Petrolemics (New York, NY: Springer New York) pp 439–68
[14] Anisimov M A, Ganeeva Y M, Gorodetskii E E, Deshabo V A, Kosov V I, Kuryakov V N, Yudin D I and Yudin I K 2014 Effects of resins on aggregation and stability of asphaltenes Energy and Fuels 28 6200-09
[15] Najafi I, Mousavi S M R, Ghazanfari M H, Ghotbi C, Ramazani A, Kharrat R and Amani M 2011 Quantifying the role of ultrasonic wave radiation on kinetics of asphaltene aggregation in a toluene–pentane mixture Pet. Sci. Technol. 29 966–74
[16] Mousavi S M R, Najafi I, Ghazanfari M H and Amani M 2012 Comparison of ultrasonic wave radiation effects on asphaltene aggregation in toluene–pentane mixture between heavy and extra heavy crude oils J. Energy Resour. Technol. 134 022001
[17] Kuryakov V, Zaripova Y, Varfolomeev M, De Sanctis Lucentini P G, Novikov A, Semenov A, Stoporev A, Gushchin P and Ivanov E 2020 Comparison of micro-DSC and light scattering methods for studying the phase behavior of n-alkane in the oil-in-water dispersion J. Therm. Anal. Calorim. 142 2035-41

[18] Kuryakov V N, Ivanova D D, Semenov A P, Gushchin P A, Ivanov E V., Novikov A A, Yusupova T N and Shchukin D 2020 Study of phase transitions in n-tricosane/bitumen aqueous dispersions by the optical method Energy & Fuels 34 5168–75

[19] Kuryakov V N and Ivanova D D 2019 Crystallization behavior of pure n-alkane (n-nonadecane) in a form of nanoemulsion Int. J. Nanosci. 18 1940032

[20] Kuryakov V N and Ivanova D D 2019 Determination of melting point of n-alkanes by means of light scattering technique J. Phys. Conf. Ser. 1385 12045

[21] Kuryakov V N, Ivanova D D and Kienskaya K I 2020 Study of the physicochemical characteristics of dispersions of n-alkanes C23H48 and C28H58 in water: zeta potential and temperatures of phase transitions Russ. Chem. Bull. 69 1306–10