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Phase Transitions in Oil Disperse Systems and their Influence on the Thermochemical Process of Oil Dehydration

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Abstract

It is established that within the temperature range of oil dehydration in the fields, a phase transition occurs in oils, accompanied by a multifold change in the particle size of their dispersed phase. The study examines the method of assessing the temperature T* at which this process occurs based on the temperature dependence of oil viscosity. It is found that with T>T*, there are two effects taking place in oils that change the stability of oil-water emulsions in two opposite directions. Specifically, the reduction of oil viscosity facilitates a decrease in emulsion stability. In turn, increased emulsion stability is promoted by a rise in the content of natural emulsifiers in the oil disperse medium at T>T* due to a phase transition with a dramatic change in the particle size of the disperse phase. Therefore, the maximum speed and degree of oil dehydration is achieved at T*, which is confirmed experimentally. As a result, the need for a critical analysis of the oil treatment temperature regime used in the fields considering phase transitions within the particles of its dispersed phase is shown.

Keywords: Oil viscosity, disperse systems, oil-water emulsions, phase transitions, the Eyring equation

1. Introduction

Problems with the preparation of oil preparation at fields worsen every year due to the involvement of previously unrecoverable high-viscosity oils in the development and the growing water content in well products. At most fields, the necessary quality of oil treatment with the required low content of water and salts is provided by using special chemical reagents and demulsifiers, as well as by heating liquid supplied to the central processing facility (CPF) up to 40-70°C. At present, all research on the optimization of this thermochemical process mostly boils down to choosing the optimal demulsifier that can ensure minimal water and salt content in the produced commercial oil at a certain temperature in the shortest time and with minimal consumption. Among the examples of such studies are the works of A.D. Agazade et al. (2019) and K.I. Matiyev et al. (2018).

At the basis of the application of heating of the fluid supplied to the CPF is the prevailing opinion among technologists that, as the viscosity of oils decreases with higher temperature, the temperature rise should provide an increase in the rate of separation of oil-water emulsions formed by them, and to a greater extent, the higher the temperature of the emulsion is (Tronov, 2000).

However, this seemingly obvious understanding of the effect of temperature on the oil preparation process requires adjustment because oils come in the form of oil disperse systems (ODS) with disperse phase particles in the form of nanoaggregates of asphaltene molecules, resins, naphthenes, and high-molecular-weight paraffins (Ganeeva et al., 2011; Safieva, 2005; Sunyaev et al., 1990; Unger, 2011; Zadymova et al., 2016). Furthermore, structural transformations and phase transitions can occur within disperse phase particles. Given that these processes lead to a change in oil viscosity, they are mostly investigated as part of addressing the problems of oil transportation. Their impact on the thermochemical process of oil preparation, however, is virtually unexplored. The present study is conducted based on this.

2. Methods

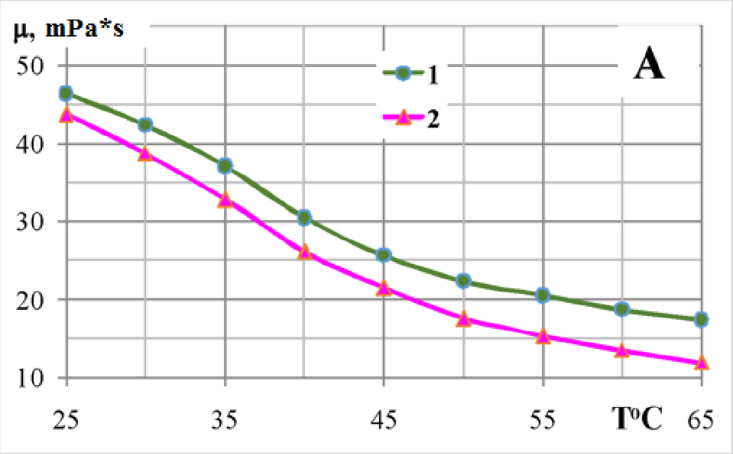
The transformations occurring in ODSs were judged based on the temperature dependence of their dynamic viscosity μ and measuring the size of particles using the method described in previous studies (Kovaleva & Semikhina, 2019; Semikhina et al., 2018, 2019). Oil viscosity **μ** was measured using a Brookfield DV-II+Pro rotational viscometer at different shear rates ν. The state of the disperse phase of ODSs was assessed using a Zetatrac (USA) laser analyzer measuring the size of particles in them.

The breakdown kinetics of ODS-based oil-water emulsions with different oil phase states were investigated using the bottle test based on the example of dehydration of 50% water emulsions. The stirring intensity of emulsions in all the compared experiments was identical and chosen to achieve their separation in 2-3 hours at the operational dosage of the demulsifier used at the oil field, based on which the emulsions under study were prepared. The reproducibility of the state of each portion of the produced emulsion was ensured by using a mechanical stirrer with a digital indication of rotation speed and automatic shutdown after a preset time.

Different phase states of ODSs for these experiments were obtained by keeping the oil samples in a sealed vessel in the thermostat at the given investigated temperature for several hours (at least 3-5 hours). The aqueous phase of the emulsion (1.5% aqueous NaCl solution) was also kept under the same conditions. At this given investigated temperature in the range of 40-70^{o}C oil-water emulsions were then produced, and their separation was studied.

3. Results and Discussion

The temperature dependencies of dynamic viscosity μ on the example of one of the studied oils in the temperature range of 20-65^{o}C presented in Figure 1 as the dependence of μ on T and lnμ on (1/T) demonstrate that similar to all the previously studied oils (Kovaleva & Semikhina, 2019; Semikhina et al., 2018, 2019) their viscosity decreases with both increasing temperature and higher shear rate. Of particular interest in identifying structural transformations in oils are the temperature dependencies of oil viscosity in Arrhenius variables, which at relatively low shear rates (ν~20-70s^{-1}) break into two linear sections with a rather sharp inflection at T* with R2>0.99 reliability (Figure 1, B).



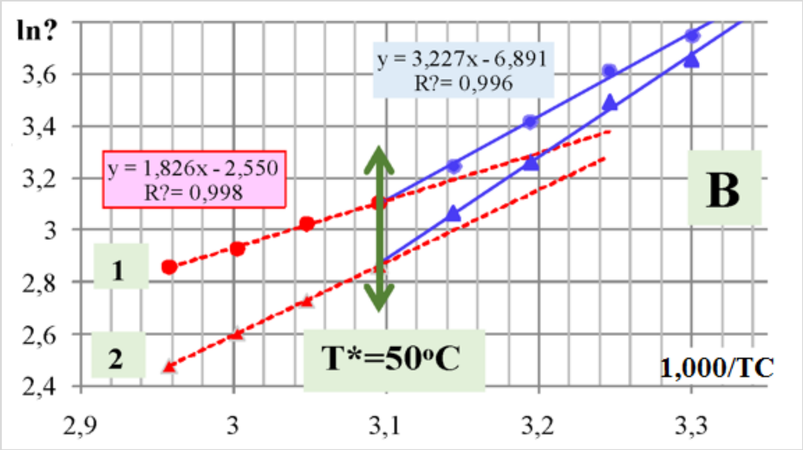


Figure 1. Temperature dependencies of oil viscosity μ in various variables at the shear rates of 26.4s^{-1} (curve 1) and 52.8s^{-1} (curve 2). The viscosity measurement error is ~1% (the size of points on the curves). For curve 1 in Figure 1 (B), the equations and reliability R^{2} of its linear approximation are also given

The presence of such inflections in the dependence of lnμ on (1/T) in various oils at T*=40±10^{o}C has been observed in several studies (Evdokimov et al., 2018; Kondrasheva & Boytsova, 2017; Kovaleva & Semikhina, 2019; Semikhina et al., 2018, 2019; Semikhina & Korovin, 2021). Their cause is believed to be a phase transition within the particles of the disperse ODS phase. Since the temperature range T*=40±10^{o}C corresponds to the melting points of some paraffins, it was assumed that the phase transition at T* in oils is determined by their melting.

However, L.P. Semikhina and S.V. Shtykov (2022) demonstrated that the crystallization temperature of paraffins in their 2-20% solutions on hydrocarbon solvents (model of the state of paraffins in oils) decreases by tens of degrees. Therefore, inflections in the dependence of lnμ on (1/T) in oils due to paraffins melting are observed in the temperature range of T<10^{o}C<T*. This conclusion is supported by data in Figure 2, according to which the content of paraffins in oil and their melting temperatures in the range of 10÷70^{o}C, which matches the oil preparation temperature, does not affect the value of T*, changing only the viscosity of oil, most strongly at low temperatures (T<T*).

Another justification of the fact that the phase transition in ODSs at T*=40±10^{o}C, which causes the inflection in the dependence of their lnμ on (1/T), is not associated with the melting temperatures of paraffins found in them is discovered in our previous studies (Kovaleva & Semikhina, 2019; Semikhina et al., 2019). It is demonstrated here that this phase transition is observed not only in oils but also in concentrated (50-98%) solutions of surfactants, with the value of T* being independent of the melting temperature of their components.

The true nature of this phase transition was investigated in our previous study (Semikhina & Shtykov, 2022). It was found to be a specific phase transition that, just like the appearance of micelles in surfactant solutions, has no equivalent at the macrolevel and exhibits the properties of both type I and type II phase transitions.

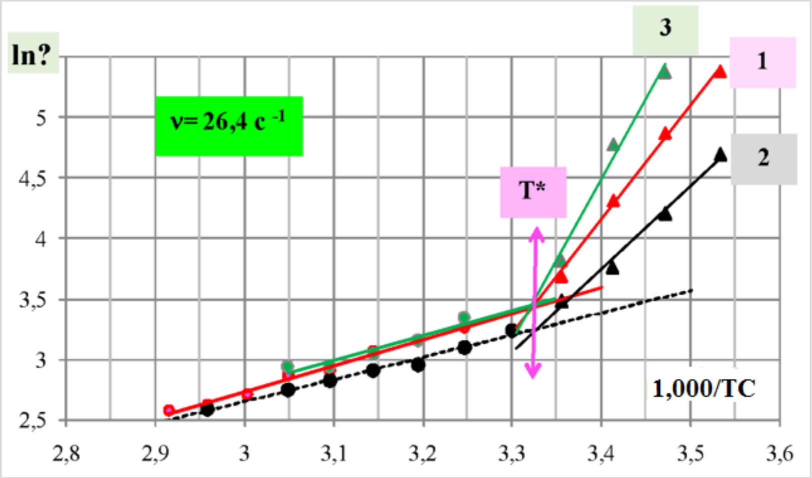


Figure 2. Dependencies of lnμ on (1/T) at the shear rate of $\nu=26.4 s^{-1}$ of the initial oil with approximately 2% paraffin content (1) and after introducing into it: 2-20% octadecane (C18) with T_{melt}~ 18°C and the molar mass of M=254 g/mol (less than the average M of oil); 3-5% paraffin with T_{melt}~ 55°C

The effect of this phase transition on the thermochemical process of oil dehydration owes to the fact that it is accompanied by a sharp change in particle size in the ODS (Figure 3). Consequently, some of the molecules of resins and high-molecular-weight paraffins present inside the ODS particles at T<T* pass into the disperse ODS, thus enriching it with reagents that present natural emulsifiers and increase the stability of oil-water emulsions (Kovaleva & Semikhina, 2019; Semikhina et al., 2018, 2019).

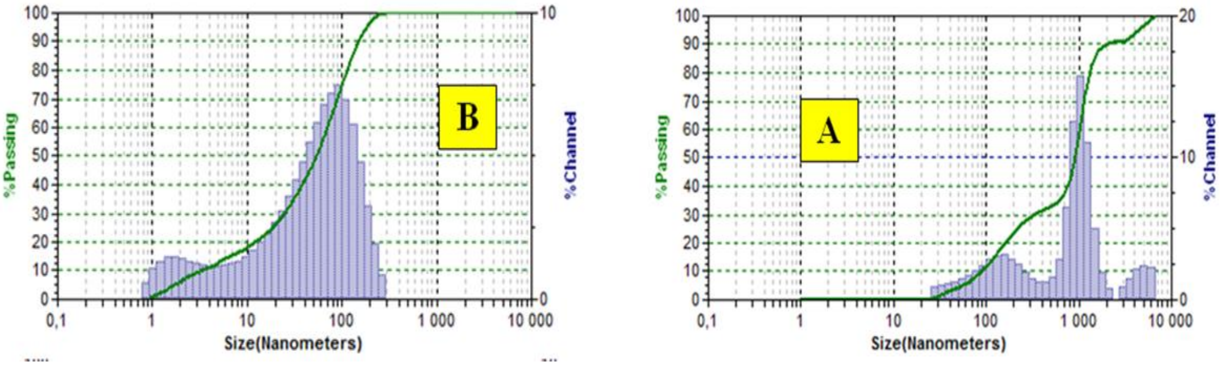


Figure 3. Characteristic particle sizes in oil at temperatures T=26°C<T* (A) and T=60°C>T* (B) on the example of oil from the Ust-Tegusskoe field

It is thus found that due to the reduction of particle size in the ODS at T>T*, two effects occur that affect the stability of the generated oil-water emulsions in two opposite ways:

1) increased stability of emulsions is promoted by a rise in the content of natural emulsifiers in the disperse ODS medium, which under T<T* are present in the oils in a bound state inside the ODS particles;

2) reduced stability of emulsions is facilitated by the reduction of oil viscosity when the temperature or shear rate rises (Figure 1).

The fact that in oils with a high content of resins, the first of these two effects may prevail, as a result of which the process of oil dehydration at elevated temperatures may not improve, but significantly worsen, is demonstrated by the experimental data in Figure 4 based on the example of the oil the viscosity temperature dependence of which is presented in Figure 1.

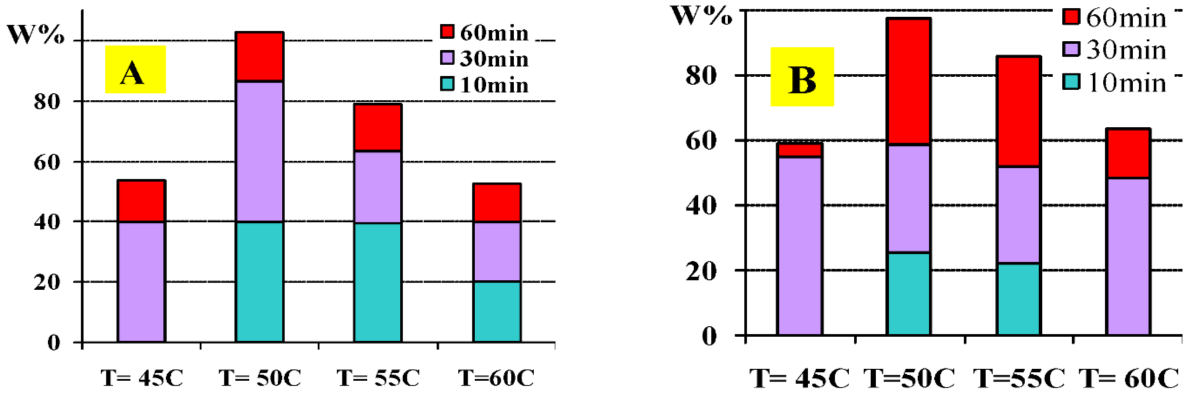


Figure 4. Diagrams of water release from 50% oil-water emulsion based on a high-viscosity oil sample after the introduction of demulsifiers RECOD-118 (A) and DIN-2E (B) at temperatures below and above T*=50°C for the given oil

The prevailing opinion among researchers that temperature increase should only elevate the rate and degree of separation of oil-water emulsions, which we shared until recently stems from the existing methodology of laboratory study of this process. The fact is that oil-water emulsions for such studies are typically prepared at room temperature around T~20-25°C from oil stored at the same temperature. The obtained emulsions are then poured into vessels, which are placed in thermostats with a certain temperature after adding demulsifiers and shaking to distribute the reagent into the emulsion. With this research methodology, the temperature dependence of the emulsion separation rate is determined only by the change in its viscosity, because within 2-3 hours, which is the typical time of experiments on the kinetics of emulsion separation, there is almost no structural rearrangement in the state of particles of the disperse phase of oils. The fact that such rearrangement is rather slow, lasting several hours (up to 15 hours), was demonstrated in our previous study (Semikhina et al., 2015). As a result, the phase state of oils in oil-water emulsions based on them is largely determined by the temperature of emulsion preparation, rather than by the temperature of their subsequent thermostatization. Therefore, in laboratory experiments, based on which the recommended parameters of operation of CPFs are established, the temperature parameters of this process at the fields should be modeled to the maximum extent possible.

A convincing example of an incorrect choice of the CPF operation mode was detected at one of the fields in the West Siberian region of Russia (Figure 5).

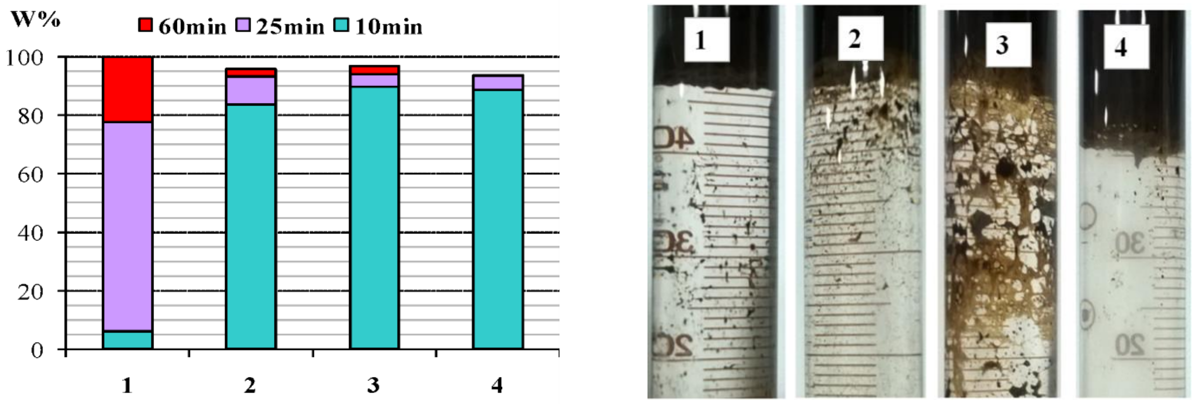


Figure 5. Diagrams of water extraction from an50% oil-water emulsion obtained from an oil sample at a temperature of 40°C≈ T* for the given oil (experiments 1 and 2) and T=70°C>T* (experiments 3 and 4): 1 and 3 – without a demulsifier; 2 and 4 – with the demulsifier used at the field with an operating

flow rate of 70g/t. The photo on the right shows the appearance of separated emulsions in experiments 1-4 after 2 hours of separation

The results of the study of 50% oil-water emulsions based on oil from the considered field (Figure 5) point to the incorrect choice of both the demulsifier and the temperature regime of oil treatment at this field. According to Figure 5, the artificial 50% emulsion produced at $40^oC \approx T^*$ almost completely separates under this temperature even without a demulsifier (experiment 1 in Figure 5). The demulsifier accelerates the separation process of this emulsion only at the initial stage, not ensuring its complete separation (experiment 2 in Figure 5).

Increasing the temperature of the oil up to $70^oC > T^*$, followed by the preparation of an oil-water emulsion from it under the same temperature and then the study of dehydration, accelerates the water extraction from the emulsion only within the first 30 min (experiment 3 in Figure 5). Then the process of water separation from the emulsion slows down, and after 1 hour the degree of oil dehydration at $70^oC > T^*$ ends up being lower than at $40^oC \approx T^*$. Photo 3 of the final appearance of the emulsion in Figure 5 demonstrates that the quality of the water produced from the oil-water emulsion also deteriorated significantly at elevated temperatures. An even greater worsening of the preparation of the studied oil at the temperature elevated to $70^oC > T^*$ occurs with the demulsifier used in the field (experiment 4 in Figure 5). The experimental results presented in Figure 5 demonstrate and identify the cause of the existing problems with oil and water treatment at some fields and indicate the high importance of correctly choosing not only the demulsifier but also the temperature mode of CPF operation, considering the phase and structural transformations of the disperse phase in oils.

4. Conclusions

The conducted experiments showed the need for a critical analysis of the temperature regimes of oil preparation used at the fields because oils are disperse systems with phase transitions in the particles of their disperse phase.

The study established the optimal temperature T^* for the thermochemical process of oil preparation, which can be determined with high accuracy by the temperature inflection point of the temperature dependence of its viscosity μ in the variables $\ln\mu$ and $(1/T)$.

It was demonstrated that at $T > T^*$ the process of oil dehydration is complicated by a phase transition with a sharp change in the size of particles in their dispersed phase and the transition of some molecules of natural emulsifiers from the bound state inside the disperse phase particles into the dispersion medium. The influence of this effect on the rate and degree of oil dehydration can exceed the effect of the reduction of oil and emulsion viscosity at higher temperatures.

In laboratory studies the temperature regime of oil-water emulsions formation and its subsequent dehydration at the CPF should be modeled as much as possible, considering that the emulsions stability is significantly dependent on the temperature of its formation due to the slow phase state transformation of oils in them.

Acknowledgments

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