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## Investigation of the interfacial tension at the interface between water and asphaltene solution in toluene

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The dynamics of the interfacial tension coefficient at the interface between water and model solutions of asphaltenes of different concentrations in toluene has been studied. It has been shown that, over time, the interfacial tension decreases due to the adsorption of asphaltene molecules at the interface. With an increase in the concentration of asphaltenes in the solution, the decrease in interfacial tension occurs more intensively. The results of a study of the elongation of a water drop in a solution under the influence of an electric field are presented. It is shown that after the formation of an adsorption film, a higher electric field must be applied to stretch the droplet, and the relative elongation depends nonlinearly on the applied voltage.

**Keywords:** interfacial tension coefficient, asphaltenes, adsorption film, drop elongation.

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Stability of water–oil emulsions is directly associated with formation of an adsorption film at the water–oil interface. Such interfacial films arise due to irreversible adsorption and aggregation of asphaltene molecules at the phase interface [1,2].

Since formation of the adsorption films and stability of oil emulsions cause specific difficulties in oil extraction, transportation and refining, many of the oil production technologies are aimed at weakening and destruction of such films.

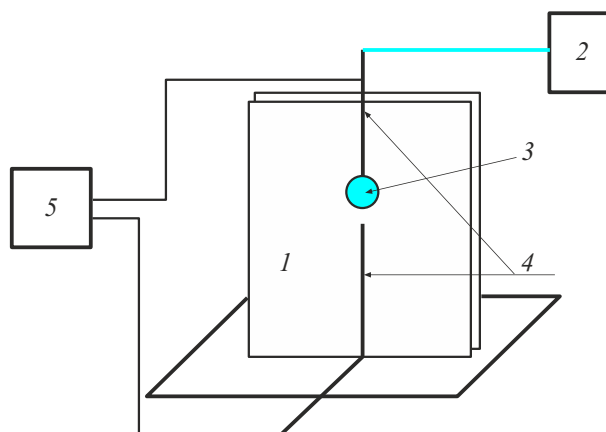
The adsorption films are characterized by certain physical properties defined by the ability of asphaltene molecules to interact with each other and to form structured adsorption layers. The most important of these properties are the interfacial tension at the phase interface, elasticity and viscosity of the adsorption film, and also duration of its formation [3–5].

The adsorption film formation needs certain time, namely, the time of establishment of the adsorption equilibrium. As particles are being adsorbed, the film properties change, and properties of the system as a whole change accordingly. Analysis by different methods of the experiments on asphaltene adsorption at the phase interface has shown that adsorption and regrouping proceed during more than 24 hours. Nevertheless, duration of the most intense processes is less than an hour [6–9]. The goal of this work was to study the dynamics of the interfacial tension at the interface between water and toluene solution of asphaltenes as well as of relative elongation of an asphaltene–coated drop.

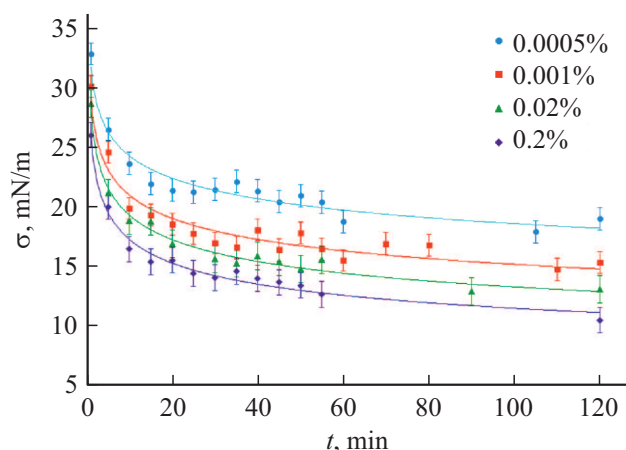
To determine the time evolution of interfacial tension at the interface between water and toluene solution of asphaltenes, the suspended drop method was used [10]. Asphaltenes were obtained by depositing from oil by *n*-heptane and multiple dissolving in toluene in order to

remove resins bound to asphaltene aggregates [11]. The model solutions of different concentrations were obtained by dissolving in toluene the extracted asphaltenes of a certain mass. Water was purified by using the Milli-Qfilter filter. The interfacial tension at the interface between water and pure toluene remained constant at the level of  $36 \pm 1$  mN/m for 10 h. All the experiments were performed at 25°C. In this work, in addition to the free interfacial tension, relative electric–field–induced elongation of a suspended drop was determined for the cases both without the film and after formation of the adsorption film.

For studying the drop shape variations, the experimental setup presented in Fig. 1 was assembled. The water drop was blown into the different–mass–concentration model toluene solutions of asphaltenes and photo–recorded during 2 h with a photo camera. Then the drop shape time



**Figure 1.** Layout of the experimental setup. 1 — vertical cell with the model solution, 2 — syringe pump, 3 — water drop, 4 — electrodes, 5 — generator.



**Figure 2.** Time variation in the interfacial tension at the interface between water and model toluene solution of asphaltenes at different mass concentrations of asphaltenes in the solution.

evolution was analyzed according to the procedure proposed in [11], and time dependences of the interfacial tension were plotted for different asphaltene concentrations in the model solution.

Fig. 2 presents the time variation in the interfacial tension at the interface between water and toluene solution of asphaltenes at different mass concentrations of asphaltenes in the solution. Fig. 2 shows that the interfacial tension decreases with time; the higher is the asphaltene concentration in the solution, the faster and higher is the decrease in the interfacial tension coefficient. The drop blowing takes up to 1 min. This is why the first shots were made in 1 min after the beginning of drop blowing. As shown in Fig. 2, a quite intense adsorption of asphaltene molecules takes place during drop blowing. For instance, when the asphaltene concentration in the solution is 0.2%, the interfacial tension coefficient decreases from 36 to 26 mN/m during 1 min.

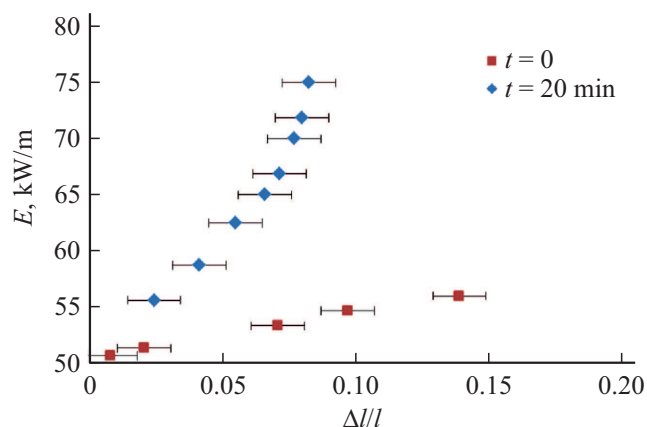
The curves show also that the most intense decrease in the interfacial tension coefficient occurs during the initial 20–30 min. After that, less intense reduction of the interfacial tension is observed. We have obtained similar results in studying the adsorption film formation at the water–oil interface by high–frequency dielectric spectrometry [9]. Therefore, in further investigations of electric–field–induced elongation of water drops with adsorption film we restricted ourselves to the time of 20 min.

The time decrease in interfacial tension may be explained by that asphaltene molecules spontaneously orientate on the phase interface surface. As a result, the difference in polarities of the adjacent phases decreases, which, according to the Rebinde’s rule, causes reduction of the interfacial tension [12]. According to the monomolecular adsorption theory [12], each active center is able to interact with only one adsorbate molecule. This means that only one layer of adsorbed molecules can arise on the surface. Upon the monolayer formation, i.e., when the optimal surface asphaltene concentration is reached, the interfacial

tension does not change. This explains insignificance of the interfacial tension variation in 20–30 min. In addition, according to the Langmuir theory, adsorption is in dynamic equilibrium with desorption. This can explain certain jumps in the interfacial tension in the right parts of the  $\sigma(t)$  curves.

Fig. 3 presents the dependences of water drop elongation on the electric field 10 kHz in frequency after keeping for 20 min in the toluene solution with the asphaltene content of 0.1%. It was shown that in 20 min the drop elongation needs application of a higher electric field, which is due to formation on the water surface of a strong adsorption film of the asphaltene molecules. The behavior of the curve for a drop with the film is similar to that of typical curves for elastic materials stretching [13]. The relative elongation of the drop with the adsorption film depends nonlinearly on the applied voltage; above the value of 0.075, the relative elongation varies insignificantly with the applied field, while in the case of a drop free of coating the curve behaves linearly.

Thus, the experimental results have shown that asphaltene adsorption on the water surface proceeds most intensely during 20–30 min at all the considered asphaltene concentrations in the solution. During this time period, there arises a stable adsorption film able to stretch like elastic materials under an applied force. The obtained results may be used in mathematical simulation of the processes of phase separation of water–oil emulsions, including those caused by electromagnetic field; they are also expected to be helpful in preparing recommendations for developing techniques for water–oil emulsion phase separation with physical fields. For instance, exposure of the emulsion to electromagnetic fields leads to weakening and destruction of the adsorption coating. If after that the drops have no time to coagulate or coalescent, the emulsions return to their initial state. Thus, in such situations it is necessary to accelerate these processes. Based on the investigation results, it is possible to predict the times of emulsion systems relaxation depending on the content of asphaltene molecules and, if necessary, recommend extra exposure methods aimed at acceleration of coagulation. Another recommendation may be given in



**Figure 3.** Relative elongation of water drops in toluene with and without the adsorption film versus the electric field.

the case of using electrohydrates in oil dehydration: in this case it is necessary to restrict the electric field depending on the strength of inhibiting coatings so as to prevent premature breakage of the coating and transition of the emulsion to a more finely dispersed state.

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### Conflict of interests

The authors declare that they have no conflict of interests.

### References

- [1] R.Z. Safieva, *Fizikokhimiya nefi* (Khimiya, M., 1998) (in Russian).
- [2] J.D. McLean, P.K. Kilpatrick, *J. Coll. Interface Sci.*, **196** (1), 23 (1997). DOI: 10.1006/jcis.1997.5177
- [3] E.M. Freer, T. Svitova, C.J. Radke, *J. Petrol. Sci. Eng.*, **39** (1-2), 137 (2003). DOI:10.1016/S0920-4105(03)00045-7
- [4] E.M. Freer, C.J. Radke, *J. Adhesion*, **80** (6), 481 (2004). DOI: 10.1080/00218460490477143
- [5] N. Aske, R. Orr, J. Sjöblom, H. Kallevik, G. Øye, *J. Dispersion Sci. Technol.*, **25** (3), 263 (2004). DOI: 10.1081/DIS-120037694
- [6] F. Baugeat, D. Langevin, R. Lenormand, *J. Coll. Interface Sci.*, **239** (2), 501 (2001). DOI: 10.1006/jcis.2001.7566
- [7] M. Jeribi, B. Almir-Assad, D. Langevin, I. Henaut, J.F. Argillier, *J. Coll. Interface Sci.*, **256** (2), 268 (2002). DOI: 10.1006/jcis.2002.8660
- [8] H.W. Yarranton, H. Alboudwarej, R. Jakher, *Industr. Eng. Chem. Res.*, **39** (8), 2916 (2000). DOI: 10.1021/ie000073r
- [9] R.R. Zinnatullin, Yu.I. Fatkhullina, I.M. Kamaltdinov, *High Temp.*, **50** (2), 298 (2012). DOI: 10.1134/S0018151X1202023X.
- [10] F.K. Hansen, G. Rødsrud, *J. Coll. Interface Sci.*, **141** (1), 1 (1991). DOI: 10.1016/0021-9797(91)90296-K
- [11] O.P. Strausz, P. Peng, J. Murgich, *Energy Fuels*, **16** (4), 809 (2002). DOI: 10.1021/ef0002795
- [12] Yu.G. Frolov, *Kurs kolloidnoy khimii. Povekhnostnye yavleniya i dispersnye sistemy* (Al'yans, M., 2004) (in Russian).
- [13] E.M. Arruda, M.C. Boyce, *J. Mech. Phys. Solids*, **41** (2), 389 (1993). DOI: 10.1016/0022-5096(93)90013-6