DOI 10.1007/s10553-020-01118-6
Chemistry and Technology of Fuels and Oils, Vol. 56, No. 1, March, 2020 (Russian Original No.1, January – February, 2020)

PECULIARITIES OF DISPERSION OF OIL RAW MATERIALS INTO AQUEOUS SOLUTIONS OF POLYCOMPLEXONES SURFACTANTS

A. Yu. Tsivadze[1], A. Ya. Fridman[1], B. P. Tumanyan[2], A. L. Maksimov[3],
A. K. Novikov[1], I. Ya. Polyakova[1], A. M. Gorbunov[1], N. N. Petrukhina[3],
and M. L. Shabanov[1]

A study was carried out on the dispersion of heavy petroleum feedstock in aqueous solutions of polycomplexon surfactants derived from triglycerides and mucopolysaccharides with and without sodium hydroxide. Up to 97.5% of the sulfur-containing compounds and up to 86% if the vanadium and nickel compounds enter the aqueous phase along with the mucopolysaccharide derivatives upon phase separation depending on the contents of surfactant and sodium hydroxide. A portion of the triglyceride derivatives remains in the petroleum phase.

Key words: *heavy petroleum, surfactants, mucopolysaccharide derivatives, demercaptization.*

The dispersion of heavy petroleum into aqueous surfactant solutions is used for demercaptization and improvement of the quality of petroleum separated from colloidal solutions [1-5]. Sulfonols and sulfonates are the major surfactants used in this process. However, these reagents do not provide for sufficient decomposition of the petroleum component complexes including those with sulfur and metal compounds. Polycomplexon surfactants have been described containing derivatives of triglycerides and mucopolysaccharides (Surf 1), which are prepared from proteincontaining waste [6]. Surf 1 has been used in the development of industrial household detergents. These products are used for highquality cleaning of containers to remove oil sludge obtained upon the isolation of petroleum from treated solutions. Hence, we

---

[1]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia/ [2]I. M. Gubkin Russian State University of Oil and Gas, Moscow, Russia. [3]A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 1, pp. 78, January – February, 2020.

undertook a study of the effect of the dispersion of heavy petroleum into solutions of Surf 1 on the change in content of sulfur and metal compounds in the petroleum separated from colloidal solutions.

In the present work, we obtained a dispersion of heavy petroleum in solutions of Surf 1 at room temperature and determined the contents of sulfur, vanadium, and petroleum after phase separation.

The samples studied were Ashalchinsk petroleum from Tatarstan containing 1.84% sulfur, 0.013% vanadium, and 0.0031% nickel. The polycomplexon reagents were from the Russian firm Tsentr containing 2.2 mmoles/g iminodiacetate derivatives (relative to dry matter) and 35% moisture.

The samples were studied by flame photometry using an FPA-01 flame photometer, optical microphotography using a Motic 300 microscope, and IR spectroscopy using a Perkin-Elmer 2000 Fourier transform spectrometer.

Weighed samples of Surf 1 and sodium hydroxide were dissolved in a glass beaker. Samples of petroleum were introduced and the mixture was stirred to give a colloidal solution not adhering to the glass beaker walls. The solution contents are given in Table 1. Microphotographs of the emulsions are given in Fig. 1.

Spherical and elliptical particles with diameter from 0.4 to 2 μm were found to predominate in the aqueous phase from solution No. 1 not containing NaOH; extended and ring-shaped aggregates constructed from these particles were also found. Needle-shaped particles with diameter 0.8-2.5 μm were found to predominate in solutions Nos. 2-4 along with fibrillar aggregates. The size and packing density of the fibrils increases with increasing NaOH concentration.

The solution separates into a petroleum phase and aqueous solution 30-40 min after preparation. The petroleum phase was separated after the establishment of equilibrium from the aqueous solution and the contents of sulfur, vanadium, and nickel were determined. The analytical data are given in Table 2.

The contents of sulfur-containing compounds as well as vanadium and nickel complexes in the petroleum sample separated out from the colloidal solution are less than in the initial sample. The extent of their extraction into the aqueous phase depends on the content of the solution, primarily on the concentration of NaOH. About 25% of the sulfur-containing compounds (relative to total sulfur) entered the aqueous phase

TABLE 1

Solution number	Crude oil, %	Surf 1, %	NaOH, %	Water, %
1	44.7	10.1	0	45.2
2	33.3	15.4	10	41.5
3	36.6	12.3	11.3	39.7
4	31.3	10.6	20.6	37.1

TABLE 2

Solution number	Content, %		
	sulfur	vanadium	nickel
1	1.38	0.0086	0.0022
2	0.377	0.0045	0.0018
3	0.0653	0.0028	0.0007
4	0.0448	0.0018	0.00048

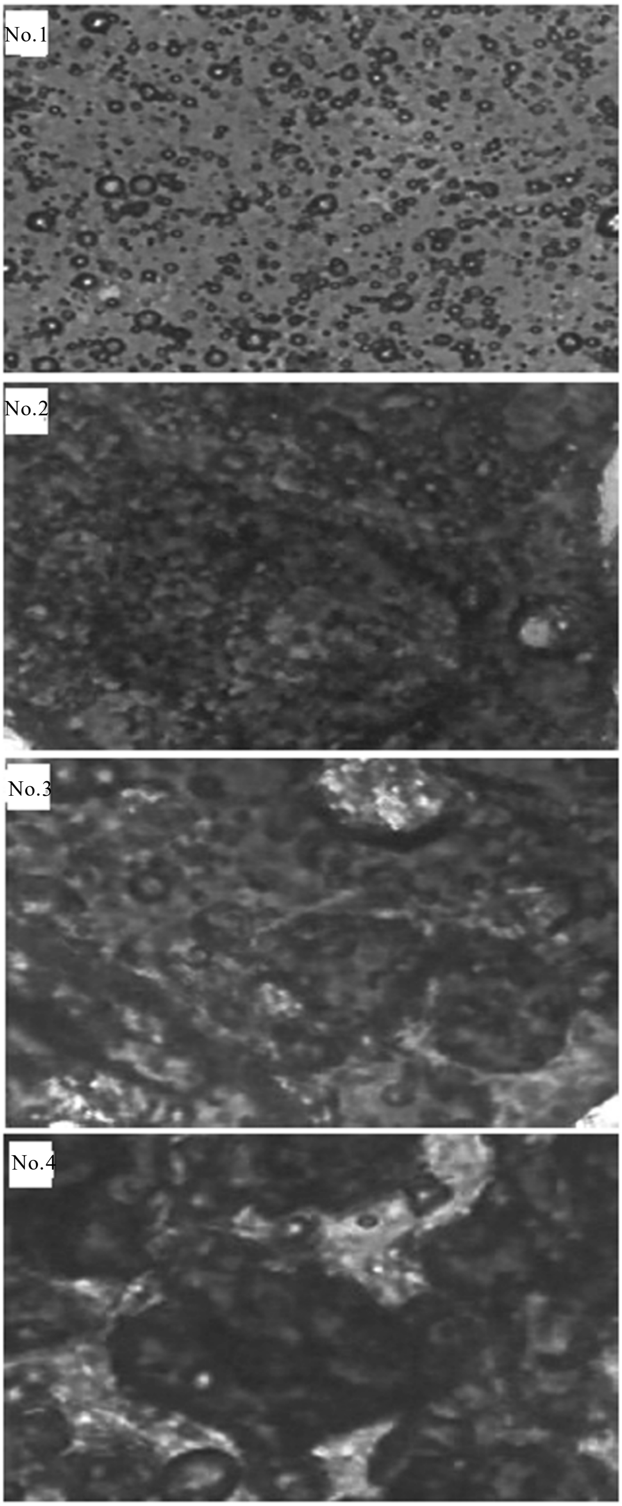

Fig. 1. Microphotographs of petroleum emulsions with reagents

from solution No. 1. The introduction of 10% NaOH led to the transfer of 78.5% sulfur-containing compounds into the aqueous phase. A further increase in the NaOH concentration to 20.6% permitted the transfer

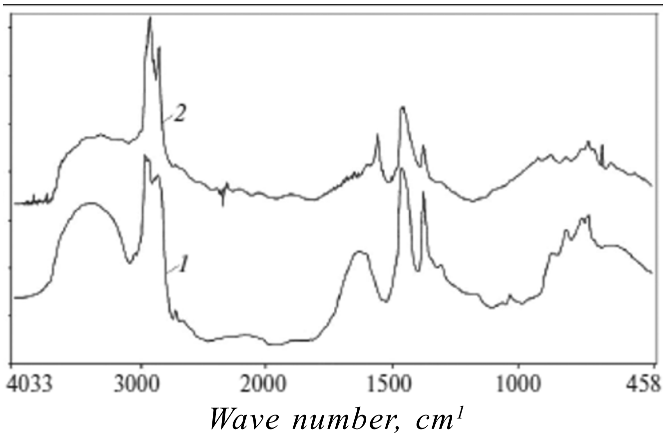

Fig. 2. IR spectra of the initial petroleum sample (*1*) and sample after treatment (*2*).

of 97.5% sulfur-containing compounds into the aqueous phase. Concurrently, up to 86% of the vanadium complexes and up to 84% of the nickel complexes (relative to the metal) were transferred to the aqueous phase.

The IR spectra of the initial petroleum sample and the samples isolated from solution No. 5 are compared in Fig. 2. The IR spectrum of the petroleum sample has a broad band at 3590-3420 cm^{-1} related to hydrogen bond vibrations, a group of bands at 3050-2900 cm^{-1} for CH bond vibrations, a band at 1640 cm^{-1} for vibrations of the C=C bonds in aromatic compounds, and a broad band at 800-550 cm^{-1} assigned to outofplane deformation vibrations of the CH bonds in tars and asphaltenes. Bands at 1723, 1232, 1150, and 1092 cm^{-1} appear in the spectrum of the treated sample corresponding to vibrations of triglyceride ester C=O and COC bonds, This spectrum also shows a band at 1597 cm^{-1} related to the NH$^+$ group and vibrations of the iminodiacetate substituent carboxyl groups [6]. Hence, derivatives of fatty acid triglycerides remain in the petroleum sample separated from the solutions.

In previous work [5], we showed that the methyliminodiacetate derivatives of the mucopolysaccharides in Surf 1 coordinate through hydrogen bonds along the chains of tri- and diglycerides to give host-guest complexes. The hydrocarbon groups in these complexes extend out in different directions. Thus, the biphilic molecules, wetting agents, and complexons are combined in Surf 1. The microphotographs of the particles of the solution of Surf 1 show that spherical particles with shells consisting of polysaccharide chains are formed upon the introduction of hydrocarbon groups of biphilic molecules into petroleum. The action of NaOH leads to breakage of the hydrogen bonds in Surf 1. Fine aggregates of petroleum components group together using biphilic molecules to give needle-shaped particles. The iminodiacetate groups become accessible to the metal complexes and sulfur-containing compounds in petroleum. The polysaccharides with bound metals transfer into the aqueous phase upon separation of the colloidal solution. Thiophene and mercaptan derivatives presumably use NaOH to associate with the polysaccharide derivatives and also pass into the aqueous phase. There is greater destruction of the hydrogen bonds in Surf 1 with increasing NaOH concentration and, thus, an increase in amount of sulfur-containing compounds and metal complexes transferred into the aqueous phase. The triglyceride derivatives, which are structurally similar to the major components of biodiesel fuel, enter the petroleum phase.

Our studies have shown the dispersion of heavy petroleum in alkaline aqueous solutions of Surf 1 holds interest for creating simple and efficient methods for demercaptization and demetallation of such products. Improvement of the petroleum quality is also possible.

This study was carried out with the financial support of the Russian Fund for Basic Research (RFFI) in the framework of Science Project No. 18-29-24137.

REFERENCES

1. T. Pekdimir, M. opur, and K. Uman, *Process Safety and Environmental Protection,* 83, No. 1, 38-46 (2005).
2. R. Kumari, A. Kakati, K. Nagarajan, et al., *Journal of Dispersion Science and Technology*, 40, No. 7, 969-981 (2019).
3. A. T. Jarullah, I. M. Mujtaba, and A. S. Wood, *Applied Energy*, 94, 182-191 (2012).
4. S. Houda, C. Lancelot, P. Blanchard, et al., *Catalysis*, 8, 1-26 (2018).
5. A. Tsivadze and A. Fridman, in: T.-M. Leticia Myriam, O. V. Kharissova, and B. I. Kharisov (editors), *Wasteless Processing of Renewable Protein and CarbohydrateContaining Waste into Consumer Goods. Handbook of Ecomaterials,* Springer (2018), pp. 1-33.
6. A. Ya. Fridman, A. U. Tsivadze, A. K. Novikov, et al., *The Scientific Method*, 1, No. 20, 25-29 (2018).