

CHEMOTOLOGY

ADDITIVE-EFFECT MECHANISM IN DISPERSE FUEL SYSTEMS

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There is no longer any doubt that all petroleum products, including diesel fuels (DF), are representatives of disperse systems, since heterogeneity and dispersivity – distinguishing signs inherent to classical disperse systems – are characteristic of them [1, 2]. For this reason, DF will hereinafter be called disperse fuel

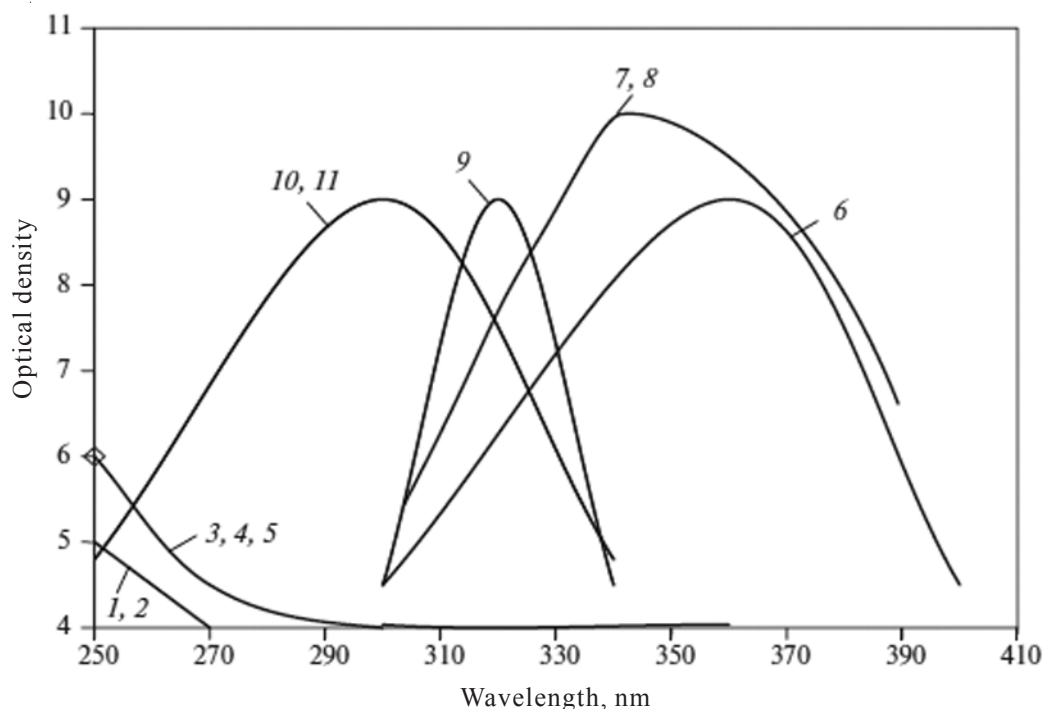


Fig. 1. UV-spectra: 1, 2) EVA and AMA-AN, respectively; 3, 4, 5) diesel fuels (DF) L, Z-35, and GShZ, respectively; 6, 9) AMA-AN and EVA, respectively, in DF L; 7, 8) AMA-AN, respectively in Z-35 and GShZ DF, respectively; 10, 11) EVA in Z-35 and GShZ DF, respectively.

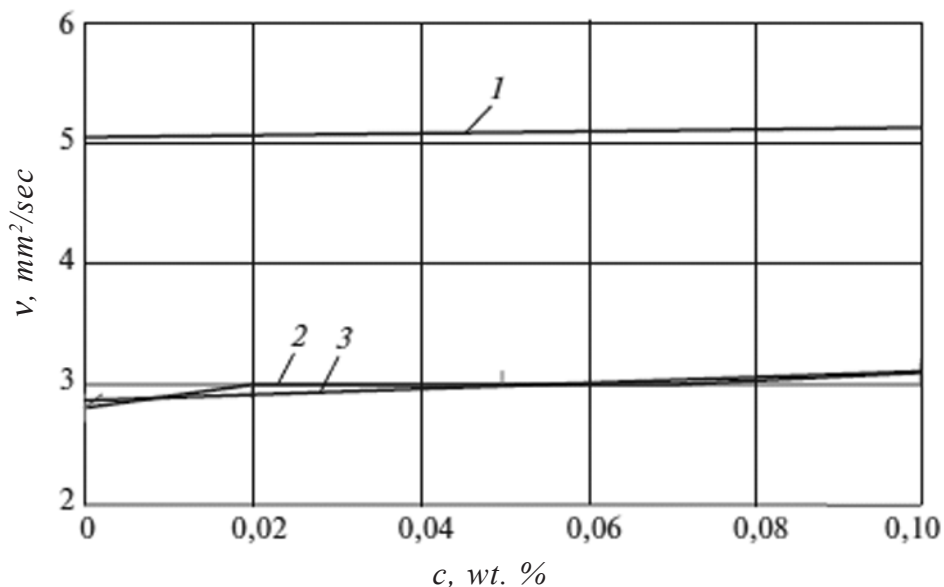


Fig. 2. Dependence of viscosity v of diesel fuels on their additive concentration:
1) L; 2) Z-35; 3) GShZ.

systems (DFS). To enhance the quality of DFS, additives of different functional purpose have already been in broad use for more than 50 years throughout the entire world [3]. There is still no single opinion, however, regarding the cause of the additive-effect mechanism in DFS.

Experimental data that we have obtained are convincing proof that intermolecular interactions (IMI) are responsible for the additive-effect mechanism in DFS. New absorption bands, which are detected by the UV method of spectral photometry in the visible region of the spectrum, but are absent in spectra of the individual components, indicate unambiguously the formation of structures of a type of complexes with transfer of charge as a result of IMI in DFS (Fig. 1).

The fact that the kinematic viscosity of DFS is independent of the concentration of additives of a different chemical nature is yet again experimental proof of IMI in DFS (Fig. 2).

Non-specific IMI were observed as early as the stage of preparation of the reactive mixture preassigned for synthesis of copolymers – depressors – by measuring the specific electrical conductance. It follows from the experimental data (Table 1) that the electrical conductance of the reactive mixture of comonomers – alkyl methacrylates of the C_{11} - C_{20} cut (AMA) and acrylonitrile (AN) is not the sum of their respective electrical conductances; in our opinion, this is convincing proof of non-specific IMI between comonomers.

Non-specific IMI most likely result in the appearance of activated molecules, interaction between which is responsible for the formation of a particular ordered copolymer structure, which, as we have demonstrated experimentally by the method of electron microscopy, assumes a “stick” conformation in DFS (Fig. 3). Moreover, we have shown that the electrical conductance of additives of various chemical structure increases with their increasing concentration in DFS. Proceeding from this, the assumption is made that interaction between additives and DFS occurs via an adsorption mechanism.

The relationship between the surface tension σ on the phase boundary of the DFS and the concentration of various additives was investigated experimentally to confirm this assumption. It was found that in all cases, the σ value of the DFS decreases with increasing additive concentration right up to its optimal value, whereupon the

Table 1

| Subject of investigation | Composition, wt. % | Specific electrical conductance $\times 10^7$, Cm/m |
|--|--------------------|--|
| AMA | 100 | 0.8400 |
| AN | 100 | 0.0056 |
| AMA + AN | 50+50 | 1.2800 |
| DFS | 100 | 0.0060 |
| AMA + DFS | 50+50 | 0.1500 |
| AN + DFS | 50+50 | 0.0055 |
| AMA + AN + DFS | 25+25+50 | 0.2834 |
| AMA-AN copolymer + DFS (50% concentrate) | 50+50 | 1.4891 |

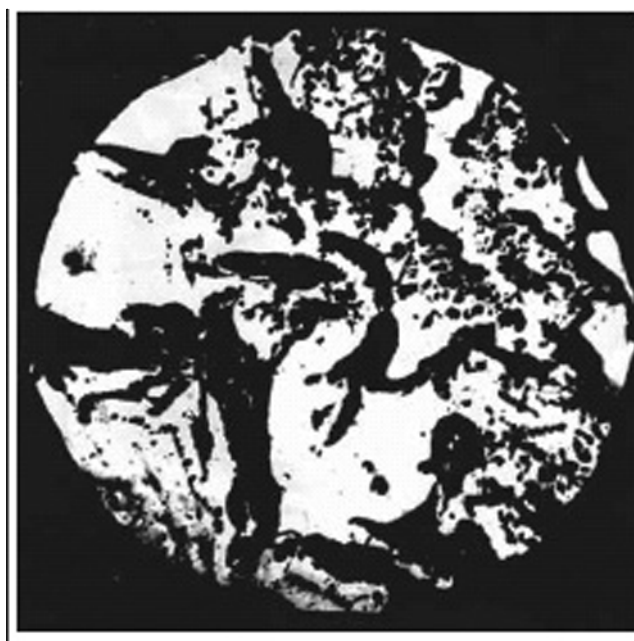


Fig. 3. Morphology of copolymer-depressor synthesized in DF medium.

greater the surface activity g possessed by the additive, the higher the value of σ (Fig. 4). Firstly, this proves that the additives under investigation belong to the class of surface active substances, and secondly, suggests an increase in the stability of DFS in the presence of the additives.

The surface activity g , which determines the ability of the substances, particularly surface-active substances, to depress the value of σ , enters into the Gibbs' adsorption equation:

$$A = Kc = -(c/RT)(d\sigma / dc) \quad (1)$$

where A is the magnitude of the adsorption, K is Henry's constant, c is the concentration of additive – surface active substance – in mole/m³, R is the universal gas constant in J/(mole \times K), T is the absolute temperature in K, $(d\sigma/dc) = g$ is the surface activity in N \times m²/mole, and σ is the surface tension in N/m.

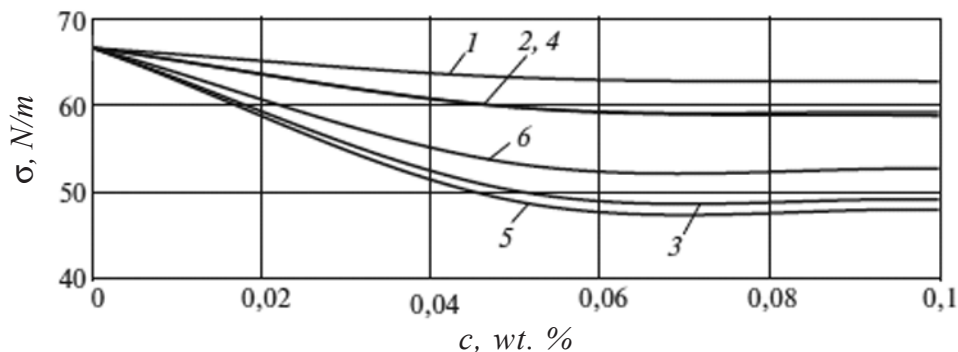


Fig. 4. Dependence of surface tension σ of diesel fuel on its additive concentration c : 1) EGN; 2) A; 3) AMA-AN; 4) ASSa; 5) SM-1; 6) EVA.

According to Henry's law, σ decreases linearly in the region of small c values with increasing c . After separation of variables in Eq. (1), and integration, we obtain

$$\sigma = \sigma_0 - KRTc$$

where σ and σ_0 are the surface tensions of the additive solution and pure solvent, respectively, at the boundary with the air.

In the region of high c values, the dependence of σ on c is nonlinear.

In both cases, the value of g is determined as the slope of the line, or tangent to the curve of the relationship in question with the opposite sign.

Values of σ and g for the additives under investigation, which were determined from the relationship $\sigma = f(c)$, are presented in Table 2 (see Fig. 4). As is apparent, all additives investigated depress the σ value of the DFS, but to different degrees. The higher the g value of the additive, the greater the reduction.

We have therefore proved experimentally that all additives investigated stabilize DFS. The greatest reduction in σ is observed in the presence of the multifunctional additive "Euroadd," which exhibits the greatest surface activity as compared with the monofunctional additives (see Table 2), and, as the tests indicated, maximum effectiveness is manifested in the DFS.

In our opinion, an increase DFS stability should result from a decrease in the average radius r of its particles, i.e., an increase in the degree of dispersivity. The average radius r of DFS particles with no additives and in the presence of additives has been determined by the optical method [4]. We had previously established the influence exerted by depressors on the increase in degree of DFS dispersivity [5]. In this study, we determined the r values of the DFS in the presence of additives with some functional purpose: cetane-increasing (A), anti-wear (B), depressor-dispersing (C), and multifunctional ("Euroadd").

As follows from the data presented in Table 3, all additives investigated reduce the r value of the DFS, whereupon the greater the surface activity g of the additive, the higher the value. The maximum decrease in r is achieved in the presence of the multifunctional additive "Euroadd," which, as the tests indicated manifests maximum effectiveness in DF. Moreover, we established experimentally that the size of the DFS particles decreases with increasing additive concentration right up to the optimal value. It should be pointed out that the greater the size reduction in DFS particles in the presence of additives, the greater the effectiveness of these additives in DF.

Thus, the experimental data that we obtained provides the basis for considering that all

Table 2

| Type of additive in DFS | c, wt. % | σ , N/m | $\Delta\sigma$, N/m | g, N \times m ² /mole |
|--|----------|----------------|----------------------|------------------------------------|
| No additive | 0 | 66.93 | — | — |
| A | 0.1 | 63.00 | 3.93 | 86.6 |
| | 0.2 | 62.80 | 4.13 | 86.6 |
| | 0.3 | 62.00 | 4.93 | 86.6 |
| B | 0.01 | 49.00 | 17.93 | 376 |
| | 0.02 | 48.80 | 18.13 | 376 |
| | 0.03 | 48.10 | 18.83 | 376 |
| C | 0.02 | 50.21 | 16.72 | 376 |
| | 0.05 | 49.20 | 17.73 | 376 |
| | 0.10 | 49.00 | 17.93 | 376 |
| Euroadd | 0.02 | 33.67 | 33.26 | 1564.3 |
| | 0.03 | 33.00 | 33.93 | 1564.3 |
| | 0.20 | 31.73 | 35.20 | 1564.3 |
| Additive designations. A – cetane-increasing; B – anti-wear; C – depressor-dispersing; Euroadd – multifunctional | | | | |

Table 3

| Type of additive in DFS | g, N \times m ² /mole | r , μ m | Δr | |
|-------------------------|------------------------------------|---------------|------------|-------|
| | | | μ m | % |
| No additive | — | 102,4 | — | — |
| A | 86,6 | 96,4 | 6 | 5,86 |
| B | 376 | 80,3 | 22,1 | 21,58 |
| C | 376 | 91,0 | 11,4 | 11,13 |
| Euroadd | 1564,3 | 75,82 | 26,58 | 25,95 |

additives – surface active substances – function in DFS on the basis of a single mechanism. The essence of the effect mechanism of additives of any functional purpose in DFS consists in increased stability of the heterogeneous system owing to a reduction in the size of the particles in its disperse phase. An increase in the degree of dispersivity of the DFS in the presence of the additives will result in improvement of its quality. The relationships obtained between the degree of dispersivity of specific DFS and the surface activity of the additives enable us to predict the effectiveness of these additives in DFS. This literally makes it possible to control quality improvement of DF by selecting familiar or newly developed effective additives to the fuels.

REFERENCES

1. Z. I. Syunyaev, R. Z. Safieva, and R. Z. Syunyaev, Disperse Petroleum Systems [in Russian], Khimiya, Moscow (1990).
2. Yu. G. Frolov, Course in Colloidal Chemistry. Surface Phenomena and Disperse Systems [in Russian], Al'yans, Moscow (2004).
3. I. N. Grishina, Physico-Chemical Bases and Laws Governing Synthesis, Production, and Use of Additives to Improve Diesel-Fuel Quality [in Russian], RGU Nefti i Gaza im. I. M. Gubkina, Moscow (2007).

4. A. N. Nesterov, Kh. M. Khaidura, Yu. I. Merezhko, et al., *Khim. Tekhnol. Topl. Masel*, No. 5, 31-32 (1988).
5. L. A. Smirnova, S. T. Bashkatova, V. A. Vinokurov, et al., *Khim. Tekhnol. Topl. Masel*, No. 1-2, 55-56 (2003).