NEW DEMULSIFIERS FOR PETROLEUM PREPARATION PROCESSES

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In preparing crude oil for refining, demulsifiers play a large role in improving the quality of petroleum products and conversion to a zero-waste system of water use in refineries (RF) [1, 2]. They are widely used in preparation of crudes in refineries and in exhaustive desalting in RF electric desalting units (EDU) [3 - 6].

The problem of breaking down stable water-oil emulsions is becoming especially acute in utilization of deposits of natural asphalts and heavy high-viscosity and high-sulfur crude oils with a high concentration of particulate contaminants. Existing technologies to intensify crude oil production using chemical reagents alter the composition of emulsion stabilizers and worsen the physicochemical and rheological properties of the feedstock produced.

Very stable water-oil emulsions and even clot-like viscous masses are formed as a result of associative interactions, and highly efficient demulsifiers are required for breaking them up [7, 8]. In refineries, mixed crude oils which frequently contain slop product and gas condensate undergo exhaustive desalting in EDU because of idle capacities. Highly efficient demulsifiers are also necessary for preparing such stock for refining.

We developed the Neftenol-D series of demulsifiers from domestic stock based on the principle of the composition of certain basic components; they satisfy current requirements and as industrial tests in plants and refineries showed, are as efficient as the foreign reagents Dissolvine, Kemelix, and Separol.

The following problems were successively solved:
- producing the fundamental components of the active base of demulsifiers of different chemical nature with optimization of the process parameters;
- finding the optimum active base of the demulsifier for real water-oil emulsions of different types of crude oil and water content;
- identifying highly efficient and the most universal composites for creating commercial forms of this series of demulsifiers.

As an analysis of the published data shows [3, 9 - 11], block copolymers based on alkylene oxides, oxyalkylated alkylphenol-formaldehyde resins, and polyesters of different chemical structures and modifications are the most promising as fundamental components of the active base of demulsifiers. Composites with different modifying additives: polyfunctional compounds with the properties of lubricants, dispersers, coagulants, flocculants, have been created from these SF.

Khimeko-GANG Co. has developed zero-waste technologies for production of SF of different chemical nature: Neftenol® BS — block copolymer of ethylene and propylene oxides with an average molecular weight of ~3000, Neftenol® KS — a product of the oxyalkylated alkylphenol-formaldehyde resin type with an average molecular weight of ~2500. It should be noted that SF of the phenol-formaldehyde resin type are not manufactured in our country, although demulsifiers containing compounds of this type in the active base are very effective both in exhaustive desalting of crude oil in refineries and in preparation of crude oil in plants.

The optimum composition of the active base of a demulsifier was determined with a special method based on the continuous correlation of the functional properties of SF with the structure, polarity, and polarizability of their molecules and with the intermolecular interactions [12]. This method was developed with methods of mathematical modeling and apparatus for design of experiments for multicomponent systems with consideration...
Fig. 1. Diagram of the change in the kinematic viscosity of a three-component system at different temperatures as a function of the composition of the system: $x_1$: Neftenol® BS; $x_2$: Neftenol® KS; $x_3$: SF of the polyether type; 1) 537.2 mm²/sec at 24°C; 2) 126.6 mm²/sec at 50°C; 3) 53.3 mm²/sec at 75°C; the regions to the right of curves 1, 2, and 3 correspond to compositions with a viscosity higher than the indicated values.

of the possible effects of the reaction between components [13].

In the given case, the system consisted of three SF of different chemical nature and polarity: Neftenol® BS, Neftenol® KS, and SF of the polyether type. Composites with this number of components are very varied and have a wide range of physicochemical properties. Differences in the chemical structure and interaction of the components predetermines the broad possibility of “fine tuning” the demulsifier to the real stabilizing layer of the water-oil emulsion.

The essence of the method consists of constructing a “composition—property” model for solving the optimization problem. The region of the experiment is a two-dimensional simplex: $x_1 + x_2 + x_3 = 1$, where $x_1$, $x_2$, $x_3$ are the mass fractions of the components in the mixture. The dependence between the composition ($x_1$, $x_2$, $x_3$) and any property ($Y_i$) of the mixture, for example, the demulsifying activity, viscosity, or solubility, is nonlinear, as experiments showed. On this basis, an incomplete cubic model of the following form was selected:

$$Y_i = a_1 x_1 + a_2 x_2 + a_3 x_3 + a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{23} x_2 x_3 + a_{123} x_1 x_2 x_3$$

The products of type $x_1 x_2$ and $x_1 x_2 x_3$ in the model describe possible binary and ternary effects of the reaction of the components of the system.

Mathematical modeling and graphic display of the “composition—property” correlation for determining a composition with a given property was performed on a computer with software specially developed in C++ language in Builder v. 3.0 software. This software runs in the Windows 95 operating system or an OS compatible with it and corresponds to Microsoft standards [14].

The experimental studies with the associated mathematical modeling allowed determining the optimum composition of the active base of the demulsifier for water—oil emulsions of different types of crude oil and different degrees of water content, both industrial and model [15]. Neftenol® BS with Neftenol® KS in the ratio of 50:50 (wt.) exhibited the greatest universality and highest demulsifying action.

The synergistic effect of the interaction was confirmed in studying the dependence of the viscosity—temperature properties on the ratio of components and spectral analysis. It follows from the “composition—property” diagram (Fig. 1) that at temperatures of 24 and 50°C, the kinematic viscosity of this