

Impact of surfactants in micro concentrations on certain properties of organic liquids as a basis for improving some oil-and-gas industry processes and properties of gasoline

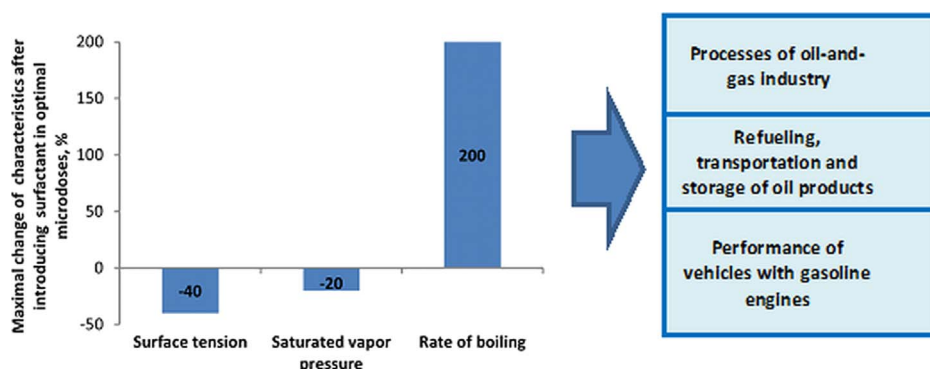


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GRAPHICAL ABSTRACT



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ABSTRACT

Surface physicochemical phenomena have a crucial role in phase interaction and in various processes in real heterogeneous systems with an advanced interfacial surface. Research into application opportunities for highly-effective surfactants in the processes of the oil-and-gas industry and the usage of petroleum products is essential. The purpose of the work is to increase the understanding of the impact of introducing surfactants in micro-concentrations on certain physical properties of multicomponent hydrocarbon systems, individual hydrocarbons and their derivatives. Patterns of the surfactants' micro concentrations effect on the surface tension, vapor pressure, boiling rate under given conditions and the rate of the phase transition "vapor-liquid" were substantiated. Recommendations on the use of surfactants in the processes of the oil-and-gas industry (rectification by various technologies, glycol dehydration of gases, adsorptive fractionation of the associated petroleum gas, storage of petroleum and light petroleum products in tanks) and the improvement of the properties of gasoline were proposed.

1. Introduction

Study of the relation between the chemical structure of surfactants

and the mechanism of their surface-active action is a fundamental scientific task which makes it possible to justify the choice of surfactants and the application conditions required for different fields. A significant

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contribution to the development of scientific fundamentals of using minor additions of surfactants to control surface phenomena and processes at the interfaces in disperse systems was made by Rehbindler [1] and his academic school. In general, the principles of physicochemical activity of surfactants are sufficiently developed at the current stage of colloid chemistry development [2–6]. However, investigations of the surfactants' action in various organic liquids including hydrocarbons and their derivatives are quite fragmentary, this being a multi-dimensional and challenging task.

For hydrocarbon systems the investigations were conducted mainly towards to emulsions [7–11]. There are some particular studies on the influence of surfactants on the physical properties of the petroleum dispersed systems. For instance, the data on changing the initial boiling point of the gasoline and diesel fractions in dependence on the concentration of surfactants introduced were presented in the study of Safieva [12].

The studies were undertaken to establish a dependence of surface tension at the surfactant/petroleum interface on the temperature, group composition and surfactant structure [13–15]. A number of publications considered the positive role of surfactants in terms of corrosion inhibition; results of studies on the mechanisms of inhibition of various types of surfactants were summarized in the review of Migahed and Al-Sabagh [16]. There are reviews summarizing the experience of the application of surfactants in the various processes of the oil-and-gas industry (e.g., the work of Bhardwaj and Hartland [17]), which concern mainly general issues of application and do not consider the mechanism of the surfactants' influence on the properties of hydrocarbon systems.

The effect of surfactants on the properties of petroleum products was considered to a greater extent in relation to the detergent properties of the related fuel additives. On the basis of representations about the mechanism of the action of additives and taking into account their ability to reduce the surface tension at the interface, laboratory methods for screening the samples were elaborated, suitable for comparison of the additives in frame of one type of chemical compounds. Different dependences of detergent properties of the fuels were obtained in response to the influence of surfactants on the surface tension [18,19].

It should be noted that the basic research towards developing fuel additives, including those having a surface active effect, are carried out principally by large companies (such as Exxon Mobil, Chevron, NewMarket Corp, Lubrisol Corp, Baker Hughes Inc, Shell, Basf AG, Honeywell Inc, The Dow Chemical Com, BP PLC). The authors of the inventions, who are the employees of companies, do not publish scientific articles and the results are presented mainly in the form of patents.

To date, systematic studies on the effect of micro concentrations of surfactants on the physical properties of organic liquids have not been carried out, the available data are not sufficient for the formation of a scientific basis for the impact of surfactants on the oil-and-gas industry processes and properties of petroleum products or developing a systematic approach to forecasting the surfactant composition to achieve the desired result. This led to this work focusing on the effects of micro-concentrations of surfactants on certain physical properties of organic liquids.

2. Materials and methods

2.1. Materials

Studies on the impact of surfactants on the surface tension of the gas-liquid interface were carried for diethylene and triethylene glycols, of no less than 99% purity, containing 5 vol% of distilled water, which corresponds to the real conditions of natural gas dehydration by glycols. The studies were also performed for the individual hydrocarbons (benzene, *n*-hexane, *n*-heptane, cyclohexane, of no less than 99% purity).

A non-leaded gasoline with a research octane number (RON) of 95, density (at 15 °C) of 740 kg/m³, that meets the EN-228-2004 requirements was used in studies of the surfactants' impact on the vapor pressure (which was equal to 54 kPa for the gasoline without the surfactant). Existent gum content (solvent washed) in the gasoline was 3 mg/100 ml. Content of olefins and aromatic hydrocarbons in the gasoline was 10 and 32 vol.% correspondingly, benzene content – 1 vol.%.

The effect of surfactants on the rate of boiling was examined for diethylene and triethylene glycols, of no less than 99% purity, containing 5 vol% of distilled water, and for the individual hydrocarbons – benzene, *n*-hexane, cyclohexane, of no less than 99% purity.

2.2. Surfactants' selection

The properties of surfactants are dependent on a balance between the lyophilic and lyophobic parts of their molecules. In addition, when choosing a surfactant to modify the properties of hydrocarbon systems it is not only the presence of the target positive effect and the absence of negative impact that should be taken into account but also the cost and availability of the raw synthesis components.

Taking into account, that synthetic fatty acids C₁₀–C₁₆ fraction is a large-tonnage petrochemical product and that its derivatives have good solubility in hydrocarbon systems, the salts of this fraction can be used to influence the properties of hydrocarbon systems.

Salts with composition of (C_nH_{2n+1}COO)₂ Me, where *n* = 9–15, Me is an element of the 10th group of the Periodic System were chosen for studies.

2.3. Methods

Surface tension was measured at 20 °C by the drop volume method (Tensiometer DVT50, KRUSS). Two parallel experiments were conducted for the basic organic liquids without surfactants and for each concentration of the surfactant introduced; deviation of the data obtained from the average value did not exceed 2%.

Saturated vapor pressure was determined according to the Reid procedure by the test method ASTM-D-323 using an apparatus for determining the saturated vapor pressure K11500 (Koehler). Two parallel experiments were carried out for the gasoline without additive and for each concentration of the surfactant introduced. Deviation of the results of measurements from the average value did not exceed 2%.

Studies on the effect of surfactants on the rate of water boil-off from the glycol-water solution and on the boiling rate of individual hydrocarbons were performed at a specified rate of heat supply. For this test a vessel with the liquid currently under study was placed into a thermostat, providing the temperature equal to 120° for the glycol-water solutions, and the temperature 10° above the boiling point of the liquid for hydrocarbons. The amount of liquid boiled out per time unit was determined from the weight of vapors condensed after passing through the Liebig condenser. The experiments were carried out twice for basic organic liquids without surfactants and for each concentration of the surfactant introduced; deviation of the results of measurements from the average value did not exceed 2.5%.

3. Results and discussion

3.1. Influence of the surfactants on the properties of hydrocarbon systems

3.1.1. Surface tension

Relation (1), derived from the well-known Gibbs' equation, provides a relation between the surface activity *G* (J·m/mol) and adsorption of the substance Γ (mol/m²), concentration *c* (mg/m³) and temperature *T* (K):

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