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INFLUENCE OF SURFACTANTS ON SURFACE TENSION AND SATURATED VAPOR PRESSURE OF HYDROCARBONS

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Abstract. Results of comparative research of non-volatile additives influence on surface tension of hydrocarbons (stalagmometric method) and on saturated pressure vapor are provided. It was shown that in hydrocarbon media with included surfactant addition weakening of surface tension on the border of liquid and gas phases and increasing of saturated vapor pressure may occur. Which allows for increase of light oil products yield in primary oil refining.

Keywords: distillation; hydrocarbons saturated vapor pressure; intermolecular interactions; surface-active substances; surface tension.

1. Introduction

Existing processes of primary oil refining do not provide a deep separation of fuel fractions and do not use the natural potential of crude oil, reducing technical and economic indicators of production.

Up to 8–10 % of light oil products commonly remain in black oil [4, 5, 11, 12, 16, 17].

Increasing of light oil extraction can be performed by vacuum distillation technology and secondary processes that can provide about 30–35 % capture of fuel fractions additionally.

But they are energy-consuming and require expensive equipment [4].

2. Research analysis

Modification of oil systems with surfactant additives and their exposure to physical factors such as electromagnetic and other fields can significantly affect their physical and chemical properties and phase transitions.

Thus, there is an extreme character of dependence of black oil's dielectric permittivity and conductivity upon the content of modifying surfactants [7].

Activating additives affect the hydrocarbon media structural and dynamic viscosity in similar way [1, 9, 16].

Formation of colloidal dispersions of micellar structure in surfactant hydrocarbon solutions was researched by X-ray [9] and light scattering techniques [9].

It was shown that insertion of modified additives in oil activates it and increases the yield of vacuum distillation up to 6–10 % [2, 3, 6, 8, 9, 15, 18].

Additives enable dispersing crude oil and improve the performance of catalytic cracking processes by reducing coke producing and increasing the yield of target products [15, 19], to improve the quality and yield of process carbon and electrode coke in the process of their obtaining [15].

We have previously shown that adding surfactants to hydrocarbon media significantly affects such an important parameter as saturated vapor pressure P_{sat} .

Including surfactants to hydrocarbon media can cause both increasing and decreasing of P_{sat} compared to initial state.

Positive effect of P_{sat} increasing is accompanied by corresponding decrease of boiling points T_{boil} and hydrocarbons distillation facilitation, which include complex of natural compounds (the most important among them is oil).

Dependences of surfactants concentration in hydrocarbon solutions upon P_{sat} and T_{boil} belong to extreme type with slope opposition of curves.

The positive effect of additives is shown with such distillation parameters as reduced initial and terminal boiling points, accelerating of distillation process under the same conditions.

Separation of light fractions in primary refining processes increases up to 10% due to surfactant including [10, 13, 14].

3. Purpose of work

For directional creation activating additives for the previous modifying oils it is important to determining essence of physical and chemical

phenomena that are observed in hydrocarbon solutions of non-volatile substances and causing an increase in selection of light fuel fractions in primary oil refining.

This work is devoted to research of intermolecular interactions in the systems: activating additive – hydrocarbon media the mechanism their action and effectiveness in primary processes of refining oil.

4. Results and Discussion

We assumed that the surfactants' effect is caused by their sorption on the border of liquid and gas phases and by weakening of interaction forces between molecules of hydrocarbon media due to dispersing effect, it may lead to decrease of surface tension and to increase of volatility.

For the purpose of this paper, as a model hydrocarbon which is contained in the light oil products and reflects their basic properties n-hexane was used - $T_{\text{boil}} = 68.7^{\circ}\text{C}$, surface tension $\sigma = 1.842 \cdot 10^{-3}\text{ N/m}$ at 20°C .

Anionic alkyl aryl sulfonate surfactant was as a non-volatile surfactant additive.

Apparatus (Fig. 1) for studying additives' influence on P_{sat} of hydrocarbon media was assembled [10, 13, 14].

Cells with pure hydrocarbon and hydrocarbon containing surfactants were kept in an air thermostat until constant value of the water column in the differential manometer had been reached, indicating a balance between hydrocarbon and its saturated vapor.

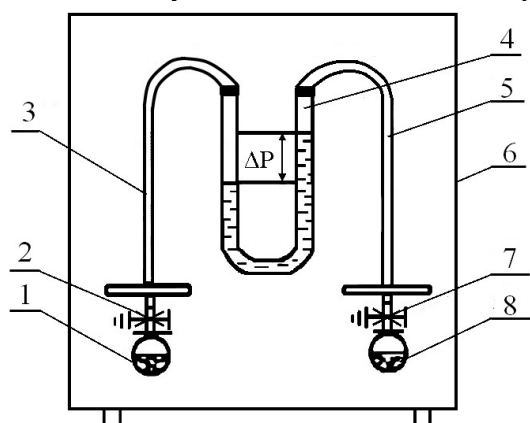


Fig. 1. Scheme of appliance for measuring difference between a saturated vapor pressure of the hydrocarbon with the additive and without:

- 1, 8 – cells with pure hydrocarbon and in presence of surfactant, respectively;
- 2, 7 – glass faucets;
- 3, 5 – thick rubber vacuum tubes;
- 4 – a water differential manometer made of glass;
- 6 – air thermostat with automatic support the set temperature and ventilator

Difference of fluid columns heights as a parameter to estimate influence of target surfactant characterizes the difference between a saturated vapor pressure of the hydrocarbon, containing certain amount of surfactant, and pure solvent in equilibrium state of both systems under the same conditions:

$$\Delta P = P_2 - P_1,$$

where P_2 , P_1 – saturated vapor pressures of hydrocarbon with surfactant and pure hydrocarbon respectively of millimeters of water column (the values ΔP were converted into Pascals).

To analyze the effect of additive on surface tension of the hydrocarbon stalagmometric method was applied.

Standard liquid with precisely known value of surface tension was used to calibrate a stalagmometer.

Drop forming time was at least 4 s.

Measurement was duplicated many times and results were averaged.

Graphical dependences of surfactant volume concentration on saturated vapor pressure of n-hexane and its surface tension are shown in Fig. 2.

Including of surfactants in certain concentrations can cause positive deviation of hydrocarbon liquids from Raoult's law and increase in saturated vapor pressure.

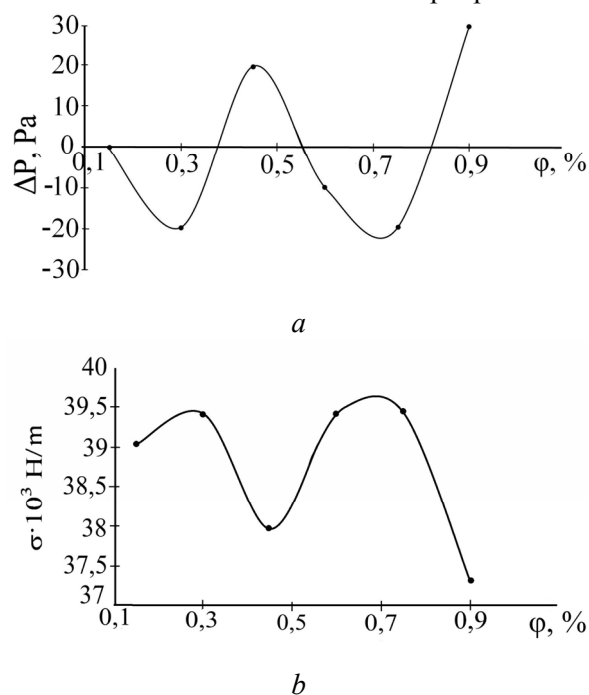


Fig. 2. Dependence of saturated vapor pressure (a) and of surface tension (b) of hexane volume concentration of surfactant

This phenomenon is typical for cases where the energy of intermolecular interactions between additive and hydrocarbon medium is less than the energy of interaction between molecules of hydrocarbon and between molecules of additives themselves and surfactants dissolving going as an endothermic process.

Dependence of additive concentration on saturated vapor pressure (ΔP) of the hydrocarbon belongs to extreme type (Fig. 2, *a*).

By increasing concentration of the solution its positive deviation from Raoult's law occurs and saturated vapor pressure increases, then effect reduces and continuously proceeds in reverse direction.

We can assume that saturated vapor pressure increase during the increasing of solution concentration occurs due to the increase of surfactant surface concentration and due to promotion of its dispersing effect on the surface layer of liquid.

That enhances dissociation of hydrocarbon molecules, associated with each other by dispersion interaction, and leads to increasing of its volatility.

On the contrary, after passing a maximum and further surfactant concentration increase, this effect is being continuously eliminated due to surfactant aggregation and micellar structures formation, as a result dispersing ability of additive reduces, which in turn reduces saturated vapor pressure.

Increasing of saturated vapor pressure of hydrocarbon in combination with non-volatile additive is accompanied by weakening of surface tension on the border of liquid and gas phases.

Dependence of dilution concentration on surface tension also belongs to extreme type.

There is a mirror similarity between dependences of surfactant concentration on surface tension and on saturated vapor pressure under the same conditions (Fig. 2, *b*).

Boiling point of hydrocarbon decreases due to increasing of P_{sat} [10, 13, 14].

Curves that illustrate slope opposed type of surfactant additives influence on saturated vapor pressure and boiling point of hydrocarbon are shown on Fig. 3.

Hydrocarbon media dispersing with surfactants gives possibilities to decrease its temperature points of beginning and ending of boiling, to accelerate distillation and to increase yield of light oil products (up to 10%) in primary oil refining [10, 13, 14].

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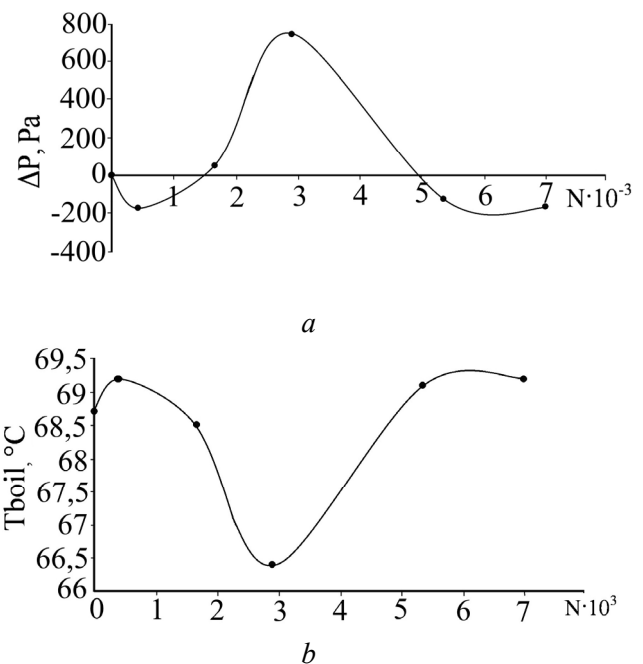


Fig. 3. Effect of surfactant concentration on the saturated vapor pressure (*a*) and boiling point (*b*) of n-hexane

The results provided in Fig. 4 can illustrate the above. Significant lowering of initial and terminal boiling points can be clearly observed there. In absence of additive, oil distillation almost stops after having risen up to 311°C.

This can be explained by a significant intermolecular attraction between the remained higher hydrocarbons and with increased surface tension of liquid phase.

It leads to saturated vapor pressure decrease.

It is required to increase temperature above 320°C to increase saturated vapor pressure up to the value, which is sufficient to continue distillation.

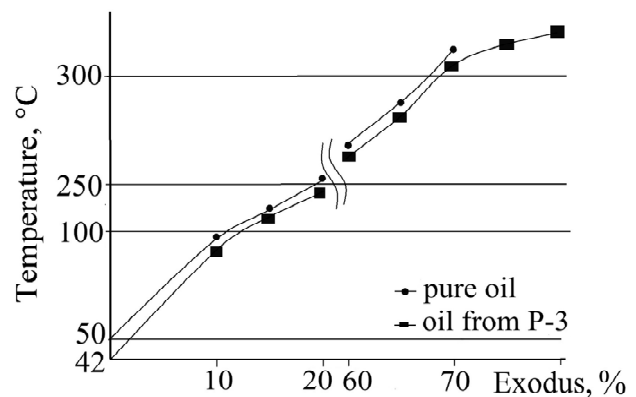


Fig. 4. Crude oil distillation curves both with inclusion and non-inclusion of surfactants

But such temperature increasing can cause hydrocarbons thermal cracking that is unacceptable for primary oil refining. But with surfactant additive included, distillation may still go on allowing additional amount of light fuel fractions to be extracted.

5. Conclusions

Small amounts of surfactants, included into hydrocarbon medium can significantly affect their surface tension and saturated vapor pressure.

Dependences of surfactant concentration on these parameters belong to extreme type and appear to be mirror-opposite to each other.

Positive deviation from Raoult's law indicates dispersing effect of additive that promotes dissociation of associated hydrocarbon molecules and as a result increases their saturated vapor pressure and lowers boiling point.

These facts make for application of surfactant to increase light oil products yield in primary oil refining.

Measurements of hydrocarbons saturated vapor pressure and surface tension (Fig. 1, 2,a) can be used for a purposeful selection of surfactants and finding their optimal concentrations with purposes to control phase transitions in hydrocarbon medium to increase productivity of primary oil refining and yield of light oil products.

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В. М. Ледовських¹, М. Б. Степанов², К.Г. Фреймантале³. Вплив поверхнево-активних речовин на поверхневий натяг і тиск насиченої пари вуглеводнів

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Розглянуто результати порівняльного дослідження впливу нелетких добавок на поверхневий натяг вуглеводнів (сталагмометричний метод) і тиску їх насиченої пари. Показано, що у присутності добавок може спостерігатися зменшення поверхневого натягу вуглеводневої рідини на межі розділу з повітрям і відповідне збільшення тиску її насиченої пари (позитивне відхилення від закону Рауля). Зазначено, що залежність цих показників від концентрації добавки має екстремальний антибатний характер, що свідчить про зменшення сил тяжіння між молекулами вуглеводнів унаслідок їх диспергування під дією добавки та зростання дисоціації асоційованих між собою за рахунок дисперсійної взаємодії молекул вуглеводневої фази. Описано, що збільшення тиску насиченої пари вуглеводневої рідини і відповідне зниження її температури кипіння дають можливість підвищувати вихід світлих фракцій нафтопродуктів у процесах первинної переробки нафти.

Ключові слова: міжмолекулярна взаємодія; перегонка; поверхневий натяг; поверхнево-активні речовини; тиск насиченої пари вуглеводнів.

В. М. Ледовских¹, Н.Б. Степанов², Е.Г. Фрейманталэ³. Влияние поверхностно-активных веществ на поверхностное натяжение и давление насыщенного пара углеводородов

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Рассмотрены результаты сравнительного исследования влияния нелетучих добавок на поверхностное натяжение углеводородов (сталагмометрический метод) и давления их насыщенного пара. Показано, что в присутствии добавок может наблюдаться уменьшение поверхностного натяжения углеводородной жидкости на границе раздела с воздухом и соответствующее увеличение давления ее насыщенного пара (положительное отклонение от закона Рауля). Отмечено, что зависимость этих показателей от концентрации добавки имеет экстремальный антибатный характер, что свидетельствует об уменьшении сил притяжения между молекулами углеводородов вследствие их диспергирования под действием добавки и возрастании диссоциации ассоциированных между собой за счет дисперсионного взаимодействия молекул углеводородной фазы. Описано, что увеличение давления насыщенного пара углеводородной жидкости и соответствующее снижение ее температуры кипения дают возможность повышать выход светлых фракций нефтепродуктов в процессах первичной переработки нефти.

Ключевые слова: давление насыщенного пара углеводородов; межмолекулярное взаимодействие; перегонка; поверхностно-активные вещества; поверхностное натяжение.

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