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METHODS OF ANALYSIS

FEATURES OF ANALYSIS OF ASSOCIATIVE HYDROCARBON MEDIA. Applicability of Refractometric Methods

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The refractive index and optical absorption of solutions of crude oil in toluene were investigated. It was found that the optical properties of systems with an extremely low content of macromolecular substances deviate significantly from Bouguer – Lambert – Beer and other laws. The sensitivity of the refractive index to association of the macromolecular components of hydrocarbon systems was revealed. To increase the accuracy of the analysis, the necessity of a detailed study of the optical properties of associative hydrocarbon systems before plotting calibration curves was demonstrated.

Refractometric methods of assessing product quality and composition are widely used in petrochemistry, and the refractive index of petroleum refining products is a quantity regulated by state standards. For this reason, great importance is attributed to the reliability of determining the broad spectrum of properties based on the refractive index.

In recent years, instrument-building companies have proposed flow analyzers for monitoring product quality in oil refineries (OR). Many domestic OR – Yaroslavl', Kirishsk, Omsk, etc. – have already introduced systems for monitoring product quality and production processes that include automated instruments – flow analyzers.

The analyzers (photometers and prismatic refractometers) are equipped with a built-in microprocessor or external computer which allows obtaining information on the manufacturing process in real time. The principle of action of most of these instruments – the flow refractometer – is based on measuring the refractive index of the medium at a certain wavelength or taking the refractometric spectrum. The instruments are tuned for operation in the visible or UV regions of the spectrum. Linear calibration curves are used to interpret the data.

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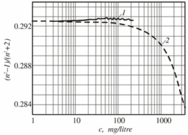

Fig. 1. Dependence of the refractive index function $(n^2 - 1)/(n^2+2)$ for a solution of crude in toluene on the concentration of asphaltenes c: 1) experimental; 2) calculated with the additive rule for ideal solutions.

Stiff requirements are imposed on the accuracy of the calibration models since the course of the manufacturing process and in the final analysis, the product (fuel) quality, are a function of the parameters measured.

The reliability of any measurements can be limited by the accuracy of the instrument, which is a function of the level of development of the engineering at the time. However, the error introduced by the method of measurement is primarily a function of the depth of the investigator's knowledge and the adequacy of the proposed calibration model. It has long been known that the widely used linear dependences of the refraction on the concentration of substance in solutions of hydrocarbons are not always valid, but the causes of the nonlinear deviations are frequently not determined.

The results of studies of the effect of the aggregate state of macromolecular compounds in crude oil on the refractive index of solutions of crude in toluene are reported here. Previously unknown features that affect the results of optical measurements were found.

Dilute solutions of crude oil in toluene were investigated in the experiments. Toluene is used as the standard solvent in optical studies of crudes and refining products. Crude from the Aznakaevo region of the Romashkino field was taken from a well in 2001 and stored in a tightly sealed container in the dark at room temperature. The concentration of asphaltenes in the crude was 3.6 wt. % and the density was 876 kg/m^3 at 20°C according to Tatneft' Co. data.

The solutions were prepared by two methods. The first method consisted of dilution of relatively large volumes of the crude in toluene. The reproducibility of the results of the measurements was unsatisfactory for solutions prepared in this way. For this reason, the second method, similar to titration, was selected to increase the reliability of the results: crude or a 5% solution in toluene was dropped into a fixed volume of toluene with a micropipette, producing solutions of accurately defined concentration. The average mass of one drop of crude coming out of the micropipette was 10.72 mg.

The optical characteristics of heavy fuels and gas condensates containing negligibly small amounts of macromolecular, polyaromatic compounds [1] are determined in the visible and UV regions of the spectrum by the presence of asphaltenes. For this reason, the composition of the solutions was subsequently characterized by the