

INVESTIGATION OF THE TEMPERATURE EFFECTS ON SUPERFICIAL TENSION IN WATER SOLUTIONS OF NEFTENOLS GF & K

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Nowadays the wide range of new chemical compounds for drilling and oil and gas recovery is supplied to the market. Comprehensive information on their properties is not available. This paper is devoted to the definition of minimum concentrations of the new domestic surfactants at ambient temperature conditions. The combined technique studying superficial and volumetric properties of solutions is described. The recommendations for agents' application are also given.

Surface active agents have a wide use both in drilling processes and in oil and natural gas production. Practice shows that exact knowledge of these agents and of their properties depending on temperature and concentration is needed. Cation surfactant "Neftenol GF" is used as drill fluid component in primary tailing-in process, it also blocks colmatage, removes bound water from the bed. Agent "Neftenol K" is used for hydrochlorid-acid treatments of bottomhole formation zones.

The aim of the research is the investigation of some relations between superficial and bulk properties of surfactants water solutions. It's also aimed at giving some practical recommendations for the tested agents.

So there are some problems with water-oil displacement when a skeleton of a rock adsorbs the main part of surfactants dissolved in a water phase. That is why it is necessary to predict surfactant losses in a bed and to determine the minimal concentrations of agents in the first portions of pumped water. We are faced with the same problems we encounter in chemical treatments of drilling fluids containing large clay solid phase with a large absorbing surface.

One should note that Neftenol GF and Neftenol K consist of a mixture of surfactants, therefore it is impossible to predict their properties theoretically [1]. Surfactants are known to be worse adsorbed in a mixture than in a single-component solution. But these are only qualitative assessments without using any formulas.

For effective managing of interface tension in oil beds we should find surfactants' critical concentrations for ambient temperature conditions. In this connection instrumental methods of phase transitions determining has a practical meaning and expands our possibilities to find an optimum solution for bed treatments.

There are several methods of critical micelle concentration (CMC) measurements. This work addresses to two of them: the surface tension isotherms technique and the refractometry.

First, interface tension of surfactants' solutions on the border with kerosene at different temperatures was determined. The stalagmometer measurements based on the drops count method [2] were carried out for water solutions of the surfactants with concentrations 0.1, 0.25, 0.5 and 1 volumetric per cent. Kerosene was taken as a model of reservoir crude oil.

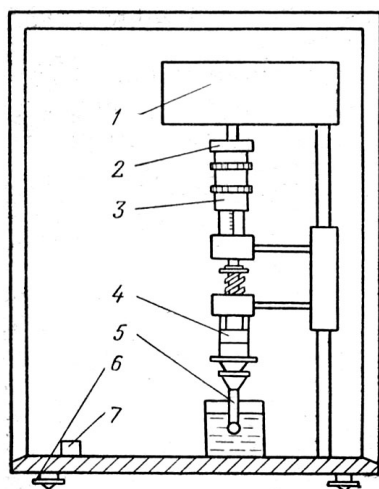


Fig. 1. Stalagmometer:
1 – electric motor; 2 – collar;
3 – micrometer; 4 – syringe;
5 – capillary; 6 – adjusting screws;
7 – level.

The method of drops count is based on the supposition that weight of a drop, tearing away from the end of the capillary, is in proportion to the superficial tension value on the bound drop – environment. In the tests drops of surfactant water solution were pressed out from a syringe 4 into purified petroleum by electric motor 1 with rotary speed 2 per minute and micro-screw pair of micrometer 3, transforming rotation to progressive motion (see *Fig. 1*). Thus a constant force acted on a piston of the syringe. The gear was thermostatted by air circulation. The system was heated only to 50°C as kerosene actively evaporates at higher temperatures. The heating took about 30 minutes.

The meaning of interface tension is defined from the following equation:

$$\sigma = \frac{V \cdot (\rho_1 - \rho_2)}{\alpha \cdot n} \cdot g ,$$

where V – total volume of drops, m³; ρ_1 and ρ_2 – densities of liquids, kg/m³; α – constant of a gear, m; n – total number of drops; g – gravitational constant, m/sec².

From the experimental results concentration and temperature dependences of interface tension were plotted. In the concentration dependence for Neftenol GF solutions (*Fig. 3*) we can distinguish some step-like peculiarities at concentrations 0,25÷0,5%. It has been also noted that the breakings smooth with temperature growth. As for the temperature dependence the curve direction

changes (Fig. 2) at the temperature of 35⁰C. For Neftenol K solutions the huge decrease of interphase tension was registered from 30 to 40⁰C. In this connection the assumption about molecules' aggregation under these conditions was put forward.

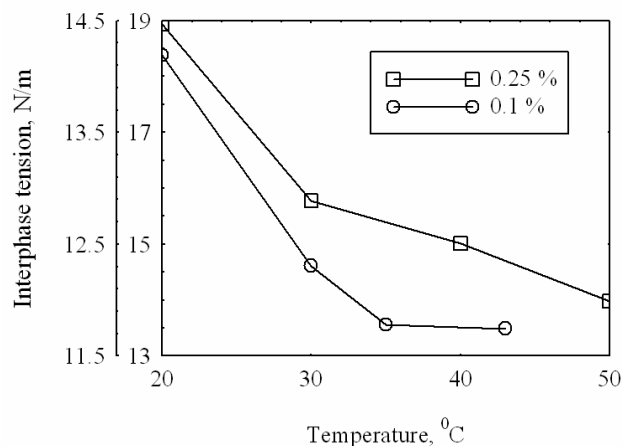


Fig. 2. Temperature dependences of interphase tension for Neftenol GF solutions.

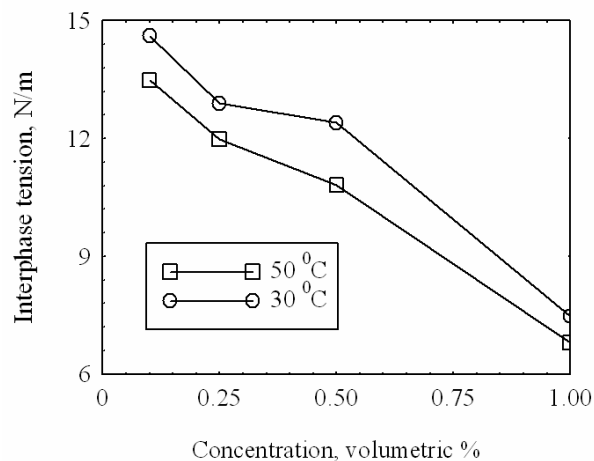


Fig. 3. Interphase tension isotherms for Neftenol GF solutions.

The refractometry technique was used for refractive index measurements. Refractometer IRF-454 B2M (Fig. 4) allows us directly measure refractive index within a wide range $n=1,2 \div 1,7$. The gear can work at different temperatures $t=10 \div 60^{\circ}C$. The wave length was limited by the red color filter KS-13 ($\lambda_{bound.} = 630nm$). The liquid thermostat ELMI-TW2.03 was connected to digital thermometer. Connecting rubber hoses of the thermostat were isolated to avoid thermal losses.



Fig. 4. Laboratory installation for refractive index measurements.

There were no significant peculiarities at temperature dependencies of Neftenol GF solutions' refractive index (Fig. 5). But if we recalculate refractive index into refraction we'll be able to apply the theory of solutions for the experimental data [4]. Refraction is different from refractive index volumetric property of solutions.

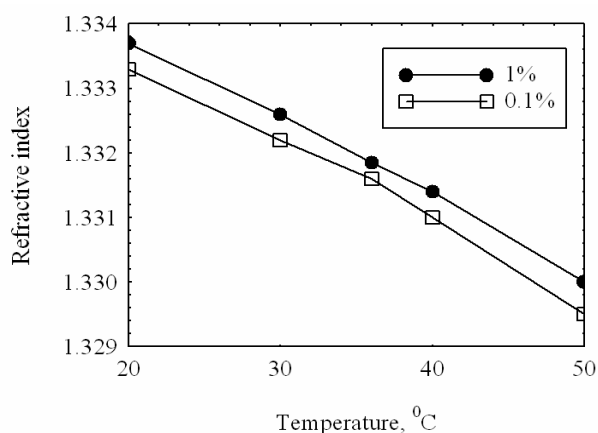


Fig. 5. Refractive index temperature dependences for Neftenol GF solutions measured by refractometer IRF-454 B2M.

Refraction of ideal solution is calculated from the equation:

$$R = \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \cdot \varphi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \cdot \varphi_2 \quad ,$$

where R – refraction of ideal solution, n_i – refractive index of a pure substance, φ_i – volumetric share of a substance.

To calculate refraction in the supposition of ideal solutions' forming pure substances (including distilled water) were tested for refractive index (*Fig. 6, 7*).

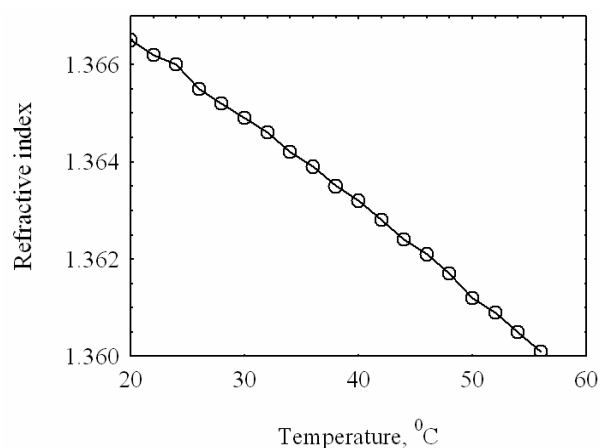


Fig. 6. Refractive index of pure Neftenol GF.

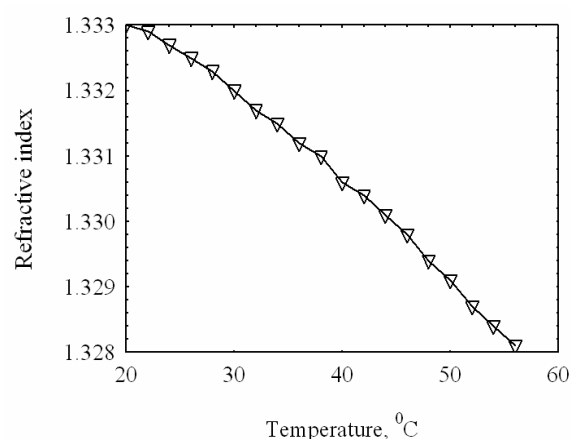


Fig. 7. Refractive index of distilled water.

For finding the refractive index values we've obtained some cubic equations from "Easy Plot" computer program. The estimated correlations are close to 1.

The experimental and theoretical curves had compared (*Fig. 8*) we found out that there is some divergence called increment of refraction:

$$RI = (R_{\text{exp}} - R)_C \quad .$$

Using refraction increment values we can estimate how the properties of a real surfactant solution differ from those of an ideal solution.

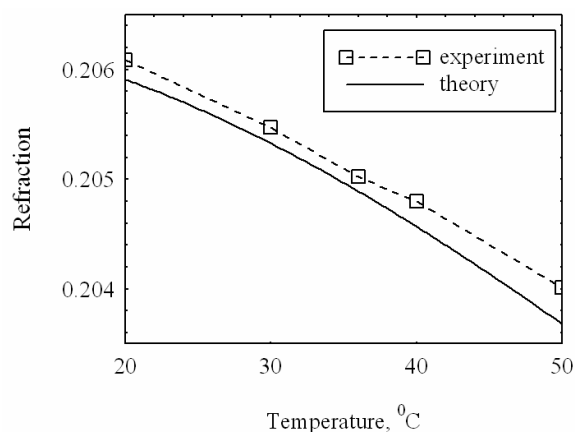


Fig. 8. Temperature dependence of refractive index of 1% Neftenol GF solution.

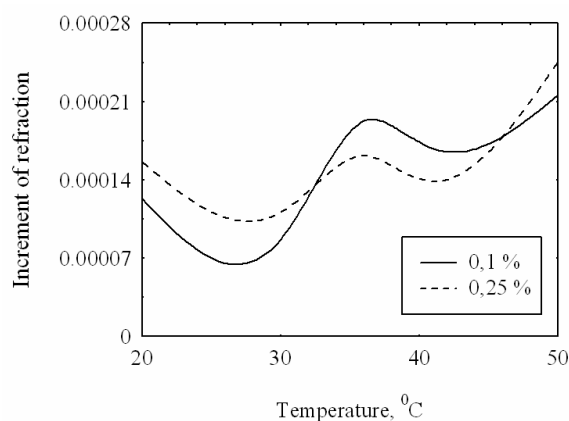


Fig. 9. Increment of refraction for Neftenol GF solutions.

As the peaks at Fig. 9 near 36°C as the interface dependences indicate some significant changes in the solutions at the pointed temperature range.

For the final estimations CMC and solubility curves were plotted. Together they form so-called phase diagram of solutions' behavior (Fig. 10).

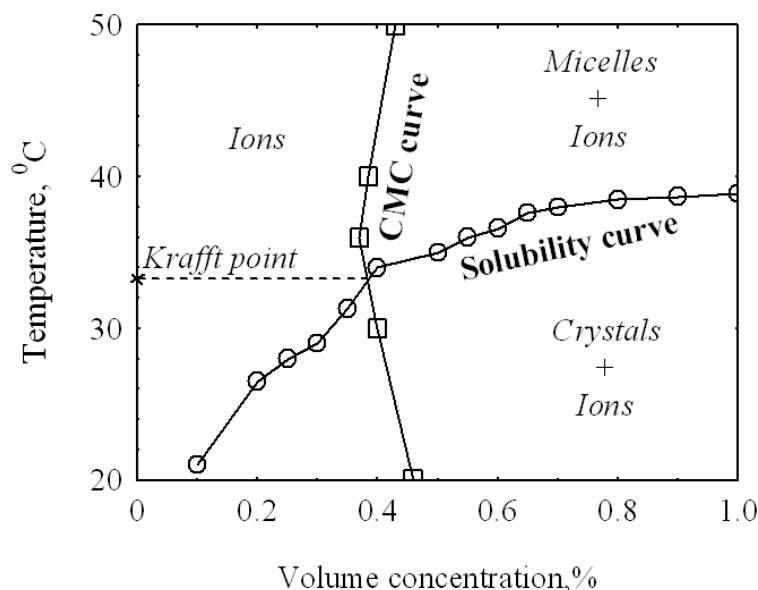


Fig. 10. Phase diagram of Neftenol GF water solutions' behavior.

The diagram analysis shows that temperature 36°C is Krafft temperature for the tested surfactants. It means that below this temperature micelles do not form, solution is saturated with monomers or crystals [3]. The suppositions about the presence of CMC in the chosen concentration range have been confirmed. CMC is about 0,3÷0,4 volumetric per cent.

Thus using the phase diagram we can develop some practical recommendations. On the one hand we should reach in practice the least value of interface tension of the penetrated liquid on the border with oil. On the other hand we shouldn't deteriorate reservoir properties by any chemical contaminations. So we should apply only micelle-containing solutions what will

provide the least value of interface tension on the bound with formation fluids even if significant adsorption takes place. In that case we can guarantee that the agent will reach the border of oil during bed treatments or influence moistening type of the rocks in drilling processes.

According to the results of the experiments it is recommended to use Neftenol GF and Neftenol K surfactants in water solutions with concentration not below 0.5 volumetric per cent and at temperatures not below 35⁰C. These conditions are of great importance as we can't apply the tested agents in several Russian oil fields. For example the mean temperatures of oil beds in Tatarstan and Bashkiria are 25÷27 degrees that is less than the determined application bound.

Thus the technique of critical concentration measurements for surfactants at real temperature conditions was developed. The connection of bulk and superficial properties of the surfactant solutions was established. Besides the recommendations for the agents' application are also given.

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