Research of inverted emulsions properties on the base of new emulsifiers

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Abstract. Emulsifiers on the base of tallol and ethanolamines derived acids have been researched in the paper. Electrical stability of emulsions drilling muds has been investigated. It is proved that synthesized emulsifiers according to emulsion stability can be divided into two groups. The first group is emulsifiers with high initial electrical stability but low emulsion stability under long-term storing, and the second group is emulsifiers with low electrical stability but with high emulsion stability. Emulsions flow characteristics have been researched. It is established that emulsifier on the base of ethanolamine provides better emulsion characteristics for drilling muds emulsions.

1. Introduction.

Oil and gas field depletion causes modification of drilling course and horizontal drilling with a large horizontal length, construction of multi-lateral wells and downhole splitters, including drilling in continental shelf waters. Under these conditions, traditional drilling muds are of little use for drilling. Emulsion drilling muds provide required drilling quantity. They permit to keep bottom-hole zone permeability, eliminate the risk of drill string drag and sidewall sticking, and provide wellbore stability as well as cutting transport [1-3].

In drilling, two types of emulsions are used: water-in-oil emulsions and oil-in-water emulsions. According to the drilling experience water-in-oil emulsions (inverted emulsions, oil-based emulsions, etc.) are good for drilling with zen more than 70°.

Oil-in-water emulsions (some types of clayless drilling mud and thin clay drilling mud) are good for drilling with zen less than 70° [4 - 5].

These groups of emulsions have both advantages and disadvantages. The strong points of hydrocarbon emulsions are low water content in filtrate and a good lubricating property. Due to these properties, hydrocarbon emulsions minimally affect productive formation, and inhibit terrigenous deposits, as well as involve drilling wells with large zen and distance.

However, hydrocarbon emulsions have a number of drawbacks, such as ecological unfriendliness to environment, instability to pollution by produced water and a great quantity of solids, dispersed phase thickening, as well as high hydraulic characteristic compared to water-based emulsions.

High content of hostile SSAS (synthetic surface active substances) in emulsion negatively affects formation fluids in some cases. Some types of oil can be thickened in a contact with SSAS. Low conductivity of hydrocarbon emulsions negatively influences on electric coring [6-9]. Thus, the urgent purpose is the formulation of emulsion muds without the drawbacks mentioned.
The paper studies inverted emulsions properties on the base of new emulsifiers and evaluation of their availability.

2. Research methodology
The authors have invented new emulsifiers on the base of tallol and ethanolamines derived acids [10]. The emulsifiers are complex mixtures of amide and ester of fatty and resin acids and some appropriate ethanolamines. Formulae of the chemical compounds according to the main components are presented in figure 1.

Figure 1. Conventional formulae of chemical compounds (R – residuum of fatty or tallol resin acid).

The main characteristic of the emulsifiers is that they have firstly been synthesized under the condition of azeotropic water distilling off with acid catalyst. The emulsifiers have been synthesized of tallol residual matter and some appropriate ethanolamines. Azeotropiser (toluene) is used to eliminate water. After distillation, toluene is put back into the mother substances. One more advantage of this method is that azeotropiser facilitates to carry out experiment under low temperature – 95 – 100 °C. Concentrated sulphuric acid is used as azeotropiser.

Emulsions include 3 components: diesel fuel, experimental emulsifier and distilled water. Initially, emulsifier was dissolved in a required amount of diesel fuel, after which small portions of water were added, and finally, this substance was being mixed by mixer Hamilton beach (13000 r/min) for 5 minutes.

Rheological properties of the emulsions were studied by viscosimeter OFITE, modification 1100. Emulsions electrical stability was measured by OFITE according to API 13B-2 [11].

3. Discussion
The purpose of the paper is to study properties of inverted emulsion on the base of mentioned emulsifier as a future base for a drilling mud. The objective of the paper is to compare the electrical stability and rheological properties of the emulsifiers and Emultal. Emultal as a comparative object is not chosen randomly. The emulsifier is a mixture of compound ester of fatty and resin acids and trietanolamine as the closest chemical product in nature. However, existing Emultal industrial technology does not infer to apply the catalyst and absorb additionally formed water.

Electrical stability is one of the important characteristics of a drilling mud. It is a complex parameter of drilling mud stability to the phase separation. Electrical stability facilitates to estimate aggregative stability of drilling mud quickly. The dependence of inverted emulsions electrical stability on the base of emulsifiers DcM, DcD, DcT and industrial Emultal model on emulsifier concentration C is studied. Electrical stability was measured immediately after emulsion obtaining. The results are shown in figure 2.
The results show that all emulsifiers are characterized by a sharp increase in inverted emulsions electrical stability with ascending emulsifier concentration up to 3%. It’s obvious that at the given concentration range the phase boundaries are saturated with emulsifier molecules, it increases aggregative emulsion stability. Under further emulsifier concentration increase, when interphase boundary is completely filled with SSAS molecules, there is a weak electrical stability rise. In this case, odd molecules of emulsifier split in the dispersion phase up as a molecular dispersion either in a form of micelles or in more complicated nematic phases, it increases dispersion phase viscosity (gel firms) as well as emulsion stability. To sum up, similar dependences are typical for the majority of emulsifiers.

The data given in figure 2, show that the researched emulsifiers in the range of standard concentrations 2 – 5% form emulsions with electrical stability of more than 220 V which makes them potentially applicable for a drilling mud. Among the three studied emulsifiers, only DcM has higher electrical stability than Emultal (if the concentration is less than 5 – 5.5%). If the concentration of DcM is more than 5 %, there is a pressure regulation of mud breakdown.

The important feature of drilling mud is emulsion stability with time. However, this parameter is rarely studied in the process of mud formulation which can lead to some difficulties in the well drilling process. Thus, the dependences of emulsions electrical stability on the concentration and time were calculated. The results are given in figure 3 (a-d).
The analysis of the dependences involves making some important conclusions: according to the data in picture 3, the studied emulsifiers can be divided into 2 groups: 1) the emulsifiers with high initial electrical stability but its fast decrease with time; 2) the emulsifiers with low initial and high time electrical stability.

The emulsifiers of the first group (DcM and Emultal) are characterized by increased electrical stability of freshly-mixed emulsions which comes to 400-600 V under 3-10% emulsifier concentration. When stored, the emulsions are broken-up quickly and their electrical stability decreases sharply.

DcM emulsifier has the fastest decrease in electrical stability with time: in 24 hours it does not exceed 90 V. The higher concentration of the emulsifier, the faster decrease in its emulsion stability is. For instance, for 0.5% emulsifier concentration, electrical stability decreases 3.3 times in 24 hours; for 3-10% emulsifier concentration, it decreases as many as 6.2–6.3 times.

Emultal has the similar features, with only the differences that the electrical stability parameters lower than 100 V are reached in 72 hours. The maximum relative decrease in electrical stability is observed in emulsions with medium emulsifier concentration (2–3%).

DcD emulsion has the similar features, with only the differences that the electrical stability parameters lower than 100 V are reached in 72 hours. The maximum relative decrease in electrical stability is observed in emulsions with medium emulsifier concentration (2–3%).

Electrical stability of freshly-mixed emulsions for emulsifiers of the second group (DcD, DcT) is in the range of 300 – 450 V under the same concentrations of 3 – 10% emulsifiers. Unlike emulsifiers of the first group, emulsifiers of the second group according to picture 3, are
characterized by high timing stability. Relative decrease in electrical stability for them is in as many as 1.3 – 3.6 times in 96 hours, whereas maximum decrease equals to average emulsifier concentration parameters (1 – 3 %). Thus, inverted emulsions based on emulsifiers DcD or DcT have rather high aggregative stability even in 96 – 120 hours.

A special feature of emulsifiers of the second group is the dependence character of electrical stability on time. In the sphere of low emulsifier concentrations, within the first hours after the emulsion formulation, its electrical stability slightly increases on average to 10-20 V. In 24 hours electrical stability of these emulsions starts slowly decreasing as mentioned above. But for emulsions with high content of emulsifier (2 – 10%), electrical stability of emulsions sharply decreases within the first hours. For medium emulsifier concentrations, electrical stability of emulsions is slightly decreasing, whereas for high emulsifier concentrations, electrical stability is slowly increasing.

Such strong changes of emulsions properties within the first hours are connected with the processes in the emulsions system structure. Firstly, there is regrouping emulsifier’s molecules in the adsorbed layer. Secondly, there is some rearrangement of the dispersion phase among globes, as a consequence of emulsion polydispersity level changes. The main process of this type is Ostwald ripening, the core of which is transportation of the dispersion phase from smaller to larger globes. Thus, the number of small globules is decreasing, whereas large globules are becoming greater in size. These processes are especially noted for emulsions with high content of emulsifier, because of emulsifier excess in the dispersion phase (due to associates or micelles), the solvability of the dispersion phase (water) increases. It is quite an unexpected fact that DcT emulsifier and Emutal have completely different dependence character between electrical stability and time. As mentioned above, Emultal refers to the first group of emulsifiers, whereas DcT – to the second group. Such a radical difference in properties seems strange, because both emulsifiers have the same chemical nature, i.e they are a tallol ester and trietanolamine mixture. It means they must be differed only by residual carboxylic acids. This problem requires further thorough study.

The research of emulsions rheological properties shows that the character of viscosity changes from emulsifier concentration is hardly depended on emulsifier properties. In all the cases the maximum of dynamic shear stress and static shear stress for DcM and DcT is 1%, for DcD – 0.5%. Decrease in drilling mud viscosity on maximum is connected with high content of emulsifiers that causes hydrocarbon phase increasing.

DcM emulsifiers produce the largest emulsions gelling, dynamic shear stress and static shear stress are about 2 times as high as DcD and DcT emulsifiers. This drilling mud has the lowest plastic viscosity that can provide a high drilling speed and a very high cutting transportation [12]. In addition, in this case drilling mud requires less emulsifier concentration. It cuts drilling well cost.

4. Summary and conclusions.

To sum up, some emulsifier properties were comparatively researched in the paper. These emulsifiers are Emultal and derived tallol and ethanolamines acids obtained under the condition of azeotropic water distilling off. Dependences between electrical stability, emulsifier concentration and their lifetime, as well as rheological properties are studied here. According to electrical stability and rheological properties, DcM emulsifier has better results in both electrical stability and rheologic properties. This mud has the least plastic viscosity that can provide a high drilling speed and a very high cutting transportation. Also, due to less concentration of emulsifier it helps to cut cost for drilling wells.
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