

Distribution of Paraffin Hydrocarbons and Asphaltenes in Acidic Water-Oil Emulsion

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Abstract—Asphaltenes and solid paraffins isolated from various layers of acidic water–oil emulsions obtained by mixing an oilfield emulsion with 15% solutions of hydrochloric and sulfamic acids with or without addition of Fe(III) have been studied by elemental analysis, IR and EPR spectroscopy, gas–liquid chromatography, and calorimetry. In acidic water–oil emulsions, the high-molecular-weight petroleum components have not been found to concentrate at the oil/water interface; however, a change in their composition has been revealed, which is more pronounced in the presence of Fe(III). The formation of diamagnetic complexes of the paramagnetic centers of asphaltenes with Fe(III) has been detected.

Keywords: asphaltenes, acidic water–oil emulsions, diamagnetic complexes

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During well operation, the reservoir properties of the bottomhole rock inevitably deteriorate as a result of clay swelling, precipitation of salts from formation water, deposition of asphaltene–resin–paraffin substances and corrosion products, formation of stable emulsions, etc. To improve the reservoir-to-well connectivity and restore rock permeability in the bottomhole formation zone (BHZ), various methods of enhanced oil recovery are used. The widest acceptance was gained by the method of well treatment with various acid compositions.

During BHZ treatment with an acid formulation, various chemical reactions occur in the rock depending on the mineralogical composition, which can result in significant quantities of sparingly soluble and insoluble inorganic products capable of precipitating and clogging the reservoir pores, thereby reducing the rate of production wells and the intake capacity of injection wells. Along with these disadvantages, a serious danger is also posed by the products of the direct interaction of acidic formulations with the petroleum fluid during the course of acid treatment. The reaction of an acid with crude oil is accompanied by the formation of stable high-viscosity emulsions and/or precipitation of organics [1–5]. These processes are greatly enhanced in the presence of ferric cations, the sources of which are the corroded surfaces of field equipment

and iron-bearing minerals of the reservoir. For a long time it was believed that organic precipitates are asphaltenic in nature, being the products of polymerization of their heterocyclic moieties in an acid medium. However, it was later shown that crude oils even with a very low asphaltene content, as well as gas condensates, can also generate organic precipitates by reacting with an acid [1, 3].

The role of Fe(III) in the deposition of organic precipitates and the formation of stable emulsions is not yet fully understood. On one hand, it is assumed that Fe(III), especially in the form of the complex HFeCl_4 , facilitates acid transfer to the oil phase, increasing the acid concentration in the oil and thereby enhancing precipitation; this assumption is confirmed by an insignificant iron content in the precipitate and by similar chemical structures of precipitates formed with and without the participation of iron [3]. On the other hand, it has been shown that Fe(III) participates in complexation with the aromatic cores of asphaltenes, causing them to flocculate into large asphaltene clusters that are unstable to deposition. Antipenko et al. [6] showed that the centers of localization of the bonding of iron ions with the organic matrix in these complexes are heteroatomic units of the molecules, free stable radicals, and vanadyl ions.