

## COMPOSITIONAL AND STRUCTURAL ANALYSIS OF OILFIELD DEMULSIFIERS USING IR AND NMR SPECTROSCOPY

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Water injection is currently implemented in most oilfields for reservoir pressure maintenance. Well fluid represents stable water-oil emulsion formed under the influence of natural surfactants contained in crude. Water separation costs comprise a large part of operating expenses for bringing produced hydrocarbons to export quality. Emulsion breaking is achieved by gravity separation and heat treatment coupled with the use of specialty chemicals – demulsifiers.

Compositional analysis is not part of the current testing protocols in operator companies for this group of oilfield chemicals, necessitating massive and laborious performance evaluations during contracting procedures. Knowledge of the chemical nature of demulsifier active components together with field application history would allow to narrow down the list of potential candidates by excluding inherently incompatible and identical products. Also important is development of robust analytical techniques for on-site quality control of commercial demulsifier batches.

This work reports the results of infrared (IR) and <sup>13</sup>C nuclear magnetic resonance (NMR) studies of the chemical composition and molecular structure of nearly 50 oilfield demulsifiers typically available from domestic suppliers.

Absorption infrared spectra were acquired in the range of 4000–650 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution by averaging over 4/64 scans on Thermo Nicolet iS5 FTIR equipped with ZnSe ATR accessory. <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> on 400 MHz Bruker Avance III. Resonance positions were measured relative to residual chloroform peak.

Commercial chemicals for immediate field application are composed of the active base respon-

sible for phase separation quality and the solvent ensuring necessary end user specifications (freezing point, pumpability, corrosivity, etc.). Demulsifier active bases were prepared by air drying at 105 °C for 2–4 hrs. Methanol-water and/or toluene mixtures were found to act as the solvent in 90 % of the samples under study; several chemicals used practically neat methanol, toluene or o-xylene.

According to the IR spectra the principal active base component of the demulsifiers were ethylene oxide-propylene oxide (EO-PO) copolymers. Olefin oxide units form polymer chains containing hydrophilic (EO)<sub>n</sub> and hydrophobic (PO)<sub>n</sub> blocks whose ratio determines polymer solubility in water and oil phases as well as interfacial tension.

In order to separate EO and PO contributions 3000–2800 cm<sup>-1</sup> C–H stretching vibration region was deconvoluted with the help of five Lorentzian functions [1]. The sum of CH<sub>2</sub> groups in both unit types is proportional to the peak magnitude at 2865 cm<sup>-1</sup> while the peak at 2969 cm<sup>-1</sup> corresponds to PO's CH<sub>3</sub> groups. Relative EO fraction in the copolymer is given by the peak height ratio A<sub>2865</sub>(CH<sub>2</sub>)/A<sub>2969</sub>(CH<sub>3</sub>). Transition from relative to absolute units was afforded by <sup>13</sup>C NMR spectra of selected active bases. Mass fraction of ethylene oxide was found to be in linear correlation with A<sub>2865</sub>(CH<sub>2</sub>)/A<sub>2969</sub>(CH<sub>3</sub>) from the IR measurements and vary between 3 % and 46 % with an average of 23 %.

ATR IR method is easy to use with minimal sample preparation. In addition to EO/PO percentages in the polymer infrared spectra provide information on terminal hydroxyl concentration, subsidiary surfactants and solvent nature, all of which critically affect demulsifier efficiency and process parameters.

### References

1. Stevanović Je., Rakitin A.R., Stojanović K. *Correlation between the Stretching Vibrations of Aliphatic Groups and the Structural and Geochemical Properties of Crude Oils of the Same*

*Genetic Type Using the Case of the Turija-Sever Oil Field, Pannonian Basin // Neftekhimiya. – 2021. – Vol. 61. – № 5. – P. 620–631.*