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Laboratory evaluation of the drag reduction additives effectiveness

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Abstract

This study describes the laboratory evaluation methodology of the drag reducing effect of block poly-1-octene. Poly-1-octene, synthesized in our laboratory was chosen as an object of the present study. To confirm the nature and the structure of the obtained polymer its FTIR spectrum was registered. The molecular mass was determined by viscosimetric method using an Ubellode viscosimeter, the obtained value was 5.22×10^6. Hydrodynamic testing of poly-1-octene solutions has been performed using a capillary rheometer of our own construction for the quantitative estimation of the polymer's drag reduction capability. We introduce criterion for a quantitative estimation of a polymer hydrodynamic drag reducing capability. This is a semi-effect concentration $C_{1/2}$ that can be determined using a dependence of DR on the concentration.

1. Introduction

An addition of the polymer, reducing a hydrodynamic drag level when pumping oil or oil-products, gives the possibilities of a facile pipework use, i.e. increasing a volume flowrate when piping through an overloaded pipeline

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section; speeding up to compensate some unavoidable losses of time; minimizing oil barges loading and unloading time; increasing a pipeline flow capacity at an offshore oil development[1].

A number of oil-soluble polymers is not too large. It includes diene caoutchoucs, amorphous polyolefins, higher polyalkyl acrylates and polyalkyl methacrylates, polyalkyl styrenes, polyvinyl alkyl ethers and some other, less available polymers. The economical justifiability of the use of a certain polymer to increase a flow capacity of an oil pipeline can be estimated taking into account its cost and efficiency. Diene caoutchoucs, polyolefins and acrylic polymers are of interest as low-cost ones. The polymers based on higher α-olefins, synthesized using a Ziegler-Natta catalyst are nowadays the leaders of almost all known oil-additives according to their cost/quality ratio among almost all of the known ones on the market since the working concentration of the polymer can be not greater than 10 ppm. Synthesis of the higher polyolefins-based polymers suitable for the use as drag reduction agents is a complicated task both in laboratory[2,3] and industrial scale[4]. In paper[3] kinetic regularities of 1-hexene polymerization, using a microspheric catalyst are considered giving a polymer suitable for the use as a drag reduction agent for light oils and petroleum-products.

All of the known oil additives can be divided into two unequal groups: soluble and suspendable ones. The soluble additives represent a solution of a polymer in a hydrocarbon liquid (such as gasoline, kerosene, etc.) The suspendable additives represent a suspension of a polymer in more polar liquids not capable to dissolve the polymer, such as alcohols, glycols, and their ether-derivatives. The suspendable additives contain a larger quantity of an active polymer (about 25 per cent) than the soluble ones do (about 10 per cent), and are much more convenient in use[1].

One of the advantageous directions in DRA evolution is the use of auto-aggregating structures. The auto-aggregation occurs where there is equilibrium between attraction and repulsion, the former being prevalent, and where the weak noncovalent interactions are functioning: van der Waals, Coulomb, hydrophobic, and hydrogen bonds. Surfactant micelles of a definite shape and supramolecular polymers can be characterized as self-organizing systems, affecting the fluids rheology. Both of them consist of monomeric units bound by the weak noncovalent bonds which can recuperate after passing a critical shifting tensions zone. In this regard they are advantageous in comparison with classic polymers in which the monomers are bound by strong chemical bonds. Polymers under these conditions are subjected to the irreversible destruction[5,6].

The mechanism of the Toms effect is still a subject of polemics[6,7].

All the variety of DRA, that has been already developed, requires a method of analysis which could give reproducible results for different polymer/solvent systems.

1.1. The Evaluation of Polymer Capability to reduce Hydrodynamic Drag Reduction towards a Hydrocarbon Liquid Turbulent Flow

The main criterion of a DRA quality is a polymeric component molecular mass (M) - the higher M is, the less a consumption of an agent supplying a definite level of a hydraulic drag reduction is. When M is less than 10^5, the polymer is not, as a rule, active as a drag reduction agent. All other things being equal, the drag reduction value is increasing symbately to a molecular mass growth.

A number of methods for the evaluation of M are known; the most popular are viscosimetry, gel-permeation chromatography[8], and light-scattering method. However, all of them are good as auxilliary ones, which give a representation of a mean value of M and of a character of a molecular-mass distribution. The most precise polymer quality estimation of a polymer as DRA can be done using a turbulence rheometer assisted by hydrodynamic testing[3,9]. The case is that a polymer's behaviour in a turbulent flow can be determined by a minimal quantity of the longest macromolecules[6,7].

Turbulence rheometers have, as a rule, not too sophisticated hardware implementation[1]. They could be arranged as coaxial cylinders, one of which is rotating, the second being driven by a liquid friction force. A rotating disc can be also used as a rheometer working unit. The equipment using a rotating unit is convenient to study polymer degradation in a turbulent flow, because they are capable to keep the flow parameters constant during a long period.

For the precise estimation of the polymer's drag reduction capability the capillary rheometers are the most suitable[9]. In such devices, using light low-viscous hydrocarbons (e.g. Oil gasoline fraction), a turbulent flow can be arranged at very low shift tensions on the wall (about several Pa). Such shift tension values (used also in industrial

pipelines) are a rigid criterion for macromolecules selection. Only molecules of super-high M values (about 10^7) can effectively reduce a hydraulic drag under conditions described above.

2. Experimental

Poly-1-octene, synthesized in our laboratory as a result of previous research works[3, 11] was chosen as an object of the present study. To confirm the nature and the structure of the obtained polymer its FTIR spectrum was registered. The spectrum of a poly-1-octene sample was registered without a solvent using a FTIR spectrometer "Nicolet 5700" within the range of 4000-600 cm^{-1}. In the spectrum of poly-1-octene, see Figure 1, some bands in the ranges of 2940 - 2915, 2870-2845, 1480-1440 cm^{-1} can be observed. They correspond to the deformation vibrations of – CH3 –bonds. The bands in the range of 1680-1620 cm^{-1}, which are specific to an unconjugated C=C bond that demonstrate the sample is monomer-free.
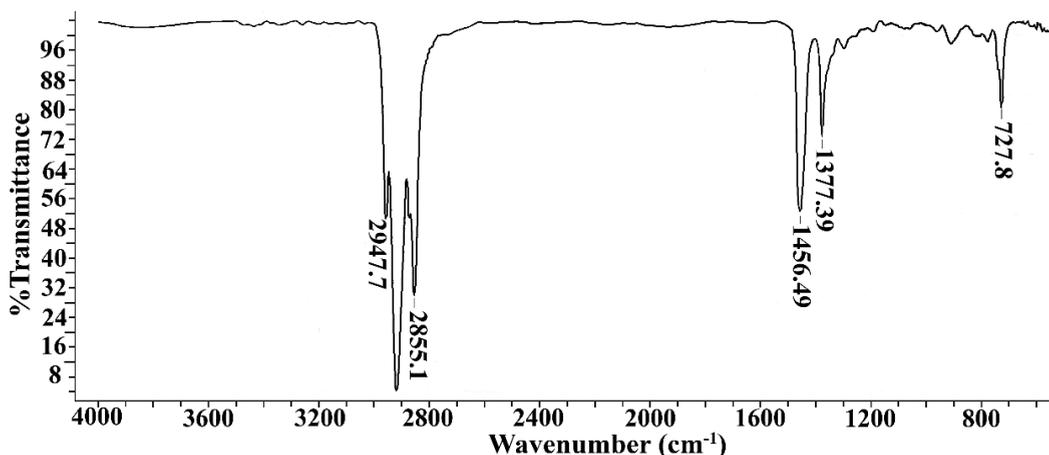

Fig. 1. FTIR spectrum of poly-1-octene.

The molecular mass was determined by viscosimetric method using an Ubellode viscosimeter, the obtained value was 5.22×10^6 (the characteristic viscosity value in tetrahydrofuran was 1.001 m^3/kg).

Hydrodynamic testing of poly-1-octene solutions has been performed using a capillary rheometer of our own construction[9].

A turbulence rheometer schematic representation is shown in Figure 2. It is similar to a viscosimeter in its construction, but it is capable to run research within a wide range of Reynolds number including both laminar and turbulent zones. The main working element of a rheometer is a heavy-wall glass pipe (*L* - its length; *D* - its diameter). The upper open end of the pipe is connected to the rheometer's working chamber filled with a liquid being studied. Through the other end supplied with a valve K4, the liquid can flow out and, further, get into a receiver. The receiver has a constant volume tank; its filling level is controlled with a photodiode sensor connected to an electronic stopwatch.
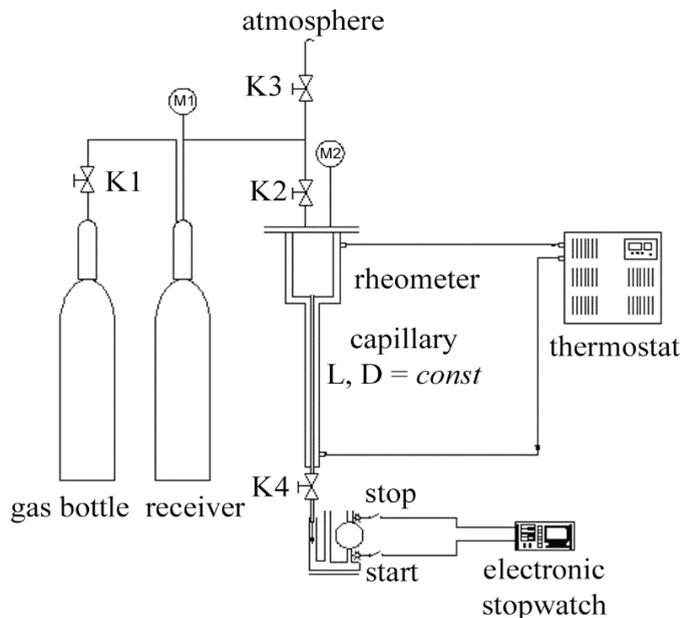
Fig.2. Turbulence rheometer schematic representation.

Using a turbulence rheometer, a discharging time is measured both for a pure solvent, e.g. straight-run gasoline (oil solvent) and then for a polymer solutions of different concentrations; the pressure changes being constant ($\Delta P_s = \Delta P_{\text{д}}$ = const).

The hydraulic drag reduction value can be calculated according to the formula (1).

$$DR, \% = (1 - t_p/t_s) \cdot 100\ \%, \tag{1}$$

where t_s - discharging time for a fixed volume of a pure solvent, t_p - discharging time for the same volume of a polymer solution; the pressure being constant.

2.1. Experimental Data Analysis

For the quantitative estimation of the polymer (or polymer-based additive) it is convenient to operate with the dependence of *DR* on an agent concentration. As a rule, this dependence represents a curve with a slightly expressed maximum, see Figure 3.
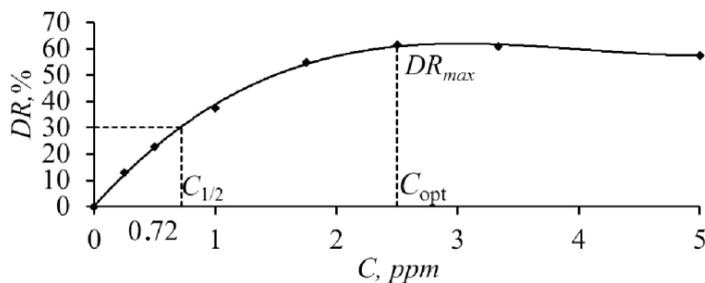

Fig.3. Dependence of the drag reduction (*DR*) on the concentration of poly-1-octene in heptane.

The comparison of the concentration curves are shown in Figure 3 for different samples gives the information about that one which is more active in drag reduction. The point marked DR_{max} corresponds to a maximal effect of hydrodynamic drag reduction[3]. A minimal concentration giving a maximal effect is an optimal concentration (C_{opt}). The maximum on a DR - C dependence curve locates in the region where a small change of the argument, comparable to the experiment allowable error, corresponds to significant change of the function, that leads to the formation of a plateau, formed with experimental data, the projection of which on an x-axis is usually comparable to or longer than that of the ascending curve segment. Thus, the estimation of C_{opt} may involve a large error. That is true also for other data presentation methods such as a dependence of a flowrate (expressed in volume units) on the polymer concentration in the solution, dependence of a flowrate increment on the polymer concentration in the solution. Such presentation data are supposed to be inconvenient for a graphical presentation of Toms effect as far as they represent absolute values, not relative ones.

For the more precise and clear estimation of the polymer activity, the DR-dependences could be presented in a number of ways. One of them is to create a chart presenting a C/DR dependence on the polymer concentration[3], DR values in per cent, C values -in part per million (ppm).

This dependence is strictly linear within the polymer low concentrations range, see Figure 4.
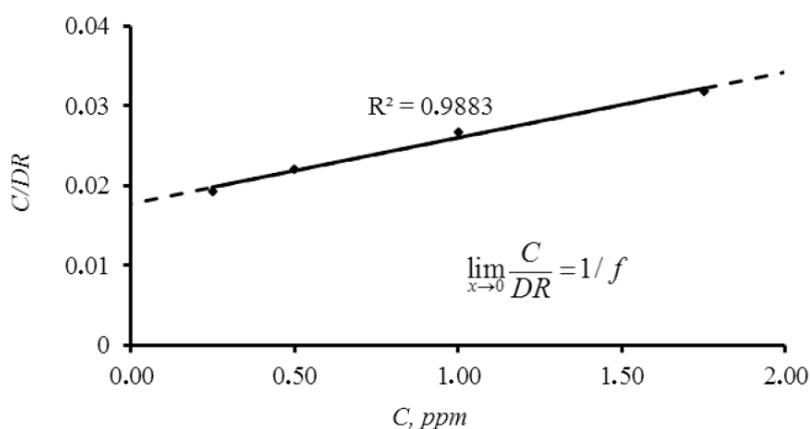

Fig.4. The concentration dependence C/DR for poly-1-octene solution in heptane.

Extrapolating the line to a zero concentration we can obtain a characteristic value of [C/DR], a reciprocal of which can be accepted as a polymer hydrodynamic efficiency f. Thus, f is a polymer molecular characteristic representing a level of drag reduction per a polymer concentration unit, the solution being infinitely diluted.

The f-parameter is a convenient criterion for a comparative estimation of different samples under constant flow conditions, and also for the estimation of the influence of any parameter of the polymer synthesis, e.g. catalyst mass content in a polymerization reaction effect on a molecular mass value, the indicator of which the value of f is.

As long as a molecular mass threshold value, from which the polymer reduces the hydrodynamic drag, is high enough, the f -parameter acquires more significance for a potential DRA molecular mass estimation compared to its characteristic viscosity, because f is only sensitive to the active in drag reduction high-molecular part of the sample. During the test-batch production for a further stand-testing it became necessary to rapidly estimate hydrodynamic characteristics of a large number of the synthesized polymer samples. As mentioned above, the estimation of DR_{max} is quite time-consuming and not too precise. Moreover, this requires the data from 5 to 7 experimental points, which means a relatively long analysis time and large solvent consumption; such charges are not always justified. The determination of a hydrodynamic efficiency f not always gives reproducible and correct results.

We introduce one more criterion for a quantitative estimation of a polymer hydrodynamic drag reducing capability. This is a semi-effect concentration $C_{1/2}$ that can be determined using a dependence of DR on the concentration, see Figure 3. In case the measurements are carried out within a quite narrow zone of shift tensions which correspond to the values in a long-distance pipeline, or at any fixed value, then the actual lab equipment has a

maximal DR value, which cannot be exceeded by any polymer of any polymer concentration. This is a device constant, which is in this case 60 per cent, see Figure 3. The concentration at which a half-value of the maximal effect can be observed (in this case it is 30 per cent) is called a half-effect concentration $C_{1/2}$, which can be assumed as an efficiency value of a present sample[12]. A sample of poly-1-octene, the data for which are presented in Figure 3, has a $C_{1/2}$, value equal to 0.72 ppm. The less $C_{1/2}$ is, the higher the polymer's capability to reduce a hydrodynamic drag to a hydrocarbon liquid flow is.

This parameter could help to monitor processes in time, e.g. polymer destruction during the storage period. During the DRA synthesis changes in a block-polymerization can be controlled, see Figure 5. The figure shows that 55-60 per cent of poly-1-octene conversion gives a minimal $C_{1/2}$, this means the optimal polymer's capability of reducing a hydrodynamic drag to a hydrocarbon liquid flow (heptane) at the actual reaction depth.

Using a dependence of *DR* on the concentration and on $C_{1/2}$ value it is convenient to comparatively estimate a DRA capability to reduce a hydrodynamic drag towards a hydrocarbon liquid flow. Figure 6 shows the concentration curves for DRA samples from four different manufacturers. As we can see, $C_{1/2}$ values are changing from 1.25 to 2.20 ppm. Taking into account that the measurement error is only about 2 per cent, we can use these data to create a gradation of DRA according to their capability to reduce a hydrodynamic drag towards a hydrocarbon liquid flow.
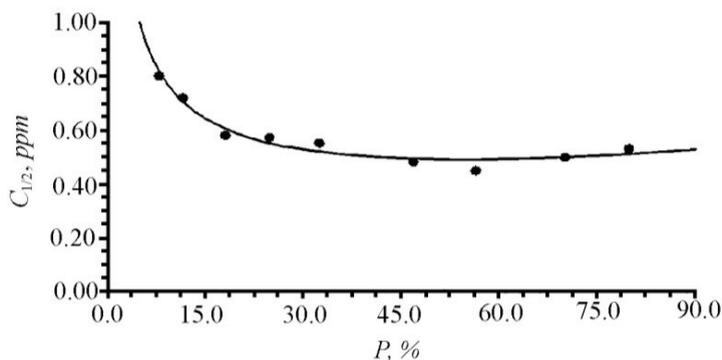

Fig.5. Dependence of the half-effect concentration $C_{1/2}$ on the conversion of poly-1-octene.
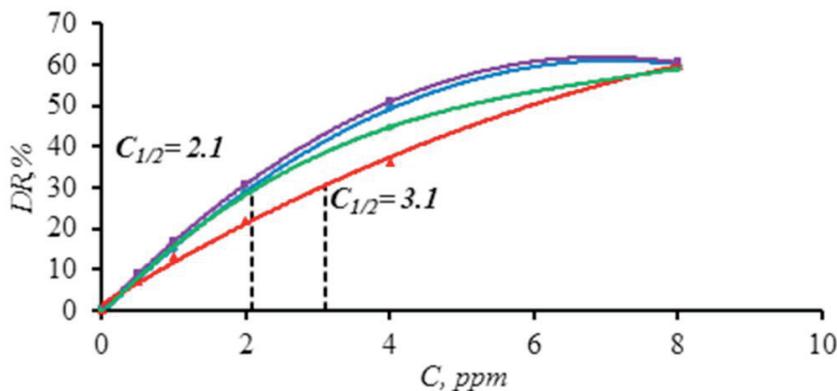

Fig.6. Concentration curves for DRA samples from four different manufacturers.

In the same manner we can monitor the additive quality from batch to batch obtained from the same supplier and the change in DRA capability to reduce a hydrodynamic drag towards a hydrocarbon liquid flow during its storage period.

3. Conclusion

The lab estimation procedure of the DRA capability to reduce a hydrodynamic drag towards a hydrocarbon liquid flow has been described. This procedure gives a possibility to create a comparative gradation of DRA from different suppliers. It also makes possible to monitor any changes in DRA capability to reduce a hydrodynamic drag towards a hydrocarbon liquid flow during the production process and during its storage period.

Acknowledgements

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