Rheological behavior of inverse emulsions of heavy crude oil

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ABSTRACT

In this work, rheological properties of water-in-crude oil emulsions in wide range of concentrations and temperatures were studied. Emulsion viscosity exponentially grows with increasing of the water content, at that the lower the temperature, the stronger this dependence appears. The nature of the flow behavior of emulsions is significantly different from crude oil. The non-Newtonian behavior is appearing at low shear rates. The relative viscosity increases with increasing emulsion concentration. Virial coefficients in the power function representing the temperature dependence of viscosity were determined. It was shown the loss modulus substantially exceeds the storage modulus that is the evidence of the liquid-like state of a material.

INTRODUCTION

Crude oil contains elevated contents of saturates, asphaltenes and resins, causing extreme flow resistance at Arctic thermal conditions due to extremely high viscosity or complex fluid rheology. Inverse water-in-crude oil emulsions are formed in the processes of crude oil transportation in the result of the mixing in the pipe at high rates. Water-in-crude oil emulsion formation is a serious issue in the petroleum transport industry. The emulsions are stabilized by natural surfactants of crude oil. The amount of water in the emulsions may vary from one oilfield to another depending on productive life of a well. The management of the rheological properties of such emulsions is a effective tool for creating new technologies of crude oil transportation.

This work is aimed to study of rheological properties of inverse emulsions based on North Sea heavy crude oil. The influence of emulsion concentration and temperature on rheological properties of emulsions was investigated.

MATERIALS AND METHODS

The dewatered acidic North Sea crude oil (19° API) was used in this study. Crude oil has been characterized into saturates, aromatics, resins, and asphaltenes (SARA) with respect to ASTM D2007 standard. The analytical data is presented in Table 1.

Distilled water (18.2 MΩ at 25 °C) was used as a water phase.

Water-in-oil emulsions (30 mL total volume) were prepared in glass vials by using a Ultra-Turrax T 25 Digital IKA with a S25N18G shaft at 8000 rpm for 5. The emulsion concentration used was 1, 5, 10, 20, 30 and 40 wt. %.

An optical microscope CX43 (Olympus, Japan) is used to obtain visual images of the prepared emulsion samples immediately after emulsification at 40X amplification. Cover glass was not placed on the samples.

Rheological properties of crude oil and water-in-crude oil emulsions were studied using the Physica MCR 302 rheometer with a cone-plate measuring cell. The cone diameter was 50 mm and the cone to plate angle was 1°. The gap between the cone apex and plate was 0.100 mm. The flow curves were obtained in the shear rate range was from 0.01 to $1\cdot100$ s^{-1}. The amplitude dependencies were obtained at constant frequency of 1 Hz at amplitude ranging from 0.01 to 100 %. Frequency dependencies were obtained in the periodic harmonic oscillation mode in the linear domain of viscoelastic behavior. The frequency range was from 0.1 to 100 s^{-1}. The amplitude of deformation was equal to 0.1%. The temperature range for all measurements was from 30 to 0 °C.

Table 1. SARA fractional of crude oil.

Parameter	Content, wt. %
Saturates	37.4 ± 0.5
Aromatics	44.1 ± 0.5
Resins	16.1 ± 0.6
Asphaltenes	2.54 ± 0.03

RESULTS AND DISCUSSION

The most critical property of emulsions is their aggregative and sedimentation stability. In our previous works[1,2] stability of water-in-crude oil emulsions were investigated using optical microscopy, Nuclear Magnetic Resonance (NMR) and Differential Scanning Calorimetry (DSC) techniques. It was shown that emulsions stay stable during the 96 hour test period without phase separation. Droplets aggregation and coalescence were also not observed. Analysis of micrographs demonstrates that average diameter of droplets in emulsion samples was approximately 4 μm (Fig. 1).

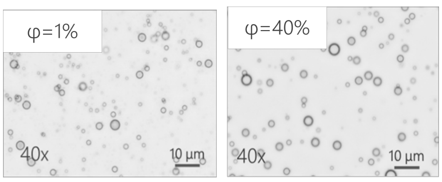

Figure 1. Micrographs of water-in-crude oil emulsions

The viscous properties of crude oil and water-in-crude emulsions were measured over a wide temperature range. The temperature dependences of viscosity of crude oil systems are presented in Figure 2. It is seen that the sample of crude oil under investigation behaves as a Newtonian fluid in the wide shear rate range, with very slight deviations from the constant viscosity values at low shear rates. This is true for the entire temperature range. Viscosity of crude oil increases with the decrease of the temperature.

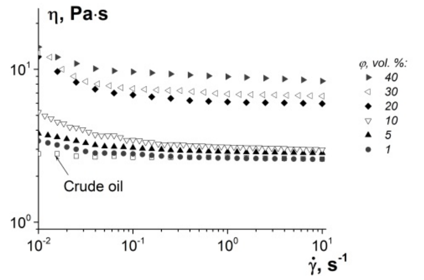

Figure 2. Flow curves of crude oil emulsions at 0 °C.

Emulsions viscosity grows with increasing of the water content, at that the lower the temperature, the stronger this dependence appears (Fig. 3). The nature of the flow behavior of emulsions is significantly different from crude oil. The non-Newtonian behavior is appearing at the shear rates from 0.001 to 1 s^{-1}, after that the viscosity becomes constant (Fig. 2). The relative viscosity increases with increasing emulsion concentration and practically does not depend on temperature (Figure 3).

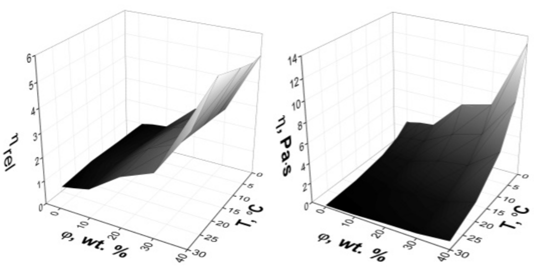

Figure 3. Temperature-concentration dependences of viscosity (η) and relative viscosity (η_r).

The power function representing the temperature dependence of viscosity can be written in the following form:

$$\eta(\varphi) = \eta_0(1 + 2.5\varphi + A_2\varphi^2 + \cdots) = \\ = \eta_0 \sum_{n=0} A\varphi^n$$

where η – viscosity of emulsion; η_0 – viscosity of continuous phase (crude oil); A_2 – the second virial Einstein coefficient.

The virial coefficients in the power function are essentially independent of temperature (Table 2).

Table 2. The values of the second virial Einstein coefficients.

T, °C	0	4	10	20	30
A_2	17±2	17±2	18±2	21±2	14±1

The viscoelastic properties of emulsions are presented by the amplitude and frequency dependencies of the dynamic modulus – storage modulus (G´) and loss modulus (G´´).

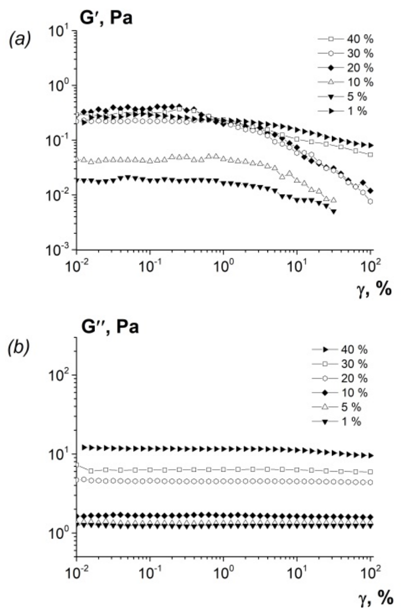

Figure 4. Amplitude dependences of G´ and G´´ at 0 °C. f = 1 Hz. Concentrations of emulsions are presented on the graph.

It was shown that a narrow region of linear viscoelasticity exists on the amplitude dependences of the viscoelastic modules of water-in-crude oil emulsions (Figure 4). At the same time, the higher the concentration of emulsion, the more narrow the domain of the linear viscoelasticity (where the G´ and G´´ values do not depend on the strain). Furthermore, the loss modulus substantially exceeds the storage modulus even for temperatures close to 0 °C.

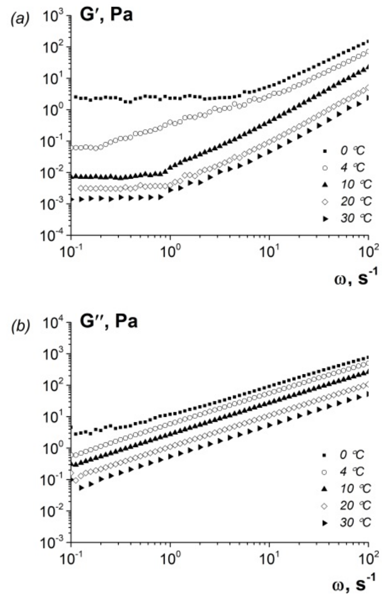

Figure 5. Frequency dependences of G´ and G´´ at different temperatures. γ = 0.1 %. φ=30 %.

The frequency dependencies of the dynamic modulus were obtained in the domain of the linear viscoelasticity (Figure 5). It is seen that G´´ exceeds G´, which shows that fluidity dominates over elasticity even at low temperatures. The difference between G´ and G´´ increases with increasing temperatures and G´´ significantly exceeds G´. The value of storage modulus increases with increasing emulsion concentration.

CONCLUSIONS

The rheological properties of stable water-in-crude oil emulsions are strongly depending on emulsion concentration and temperature. Emulsion viscosity grows with increasing of the water content, and the lower the temperature, the stronger this dependence appears. Crude oil emulsions demonstrate the non-Newtonian behavior at low shear rates. The dynamic measurements have shown that water-in-crude oil emulsions exhibit a liquid-like behaviour even at low temperatures.

ACKNOWLEDGMENTS

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