



Short Communication

Why does the viscosity of waxy oil decrease with the decrease in the cooling rate? A model



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ABSTRACT

Waxy oil is a structuring medium due to crystallization of the paraffin components on cooling. Crystallization is a rather slow kinetic process. So the degree of crystallinity depends on the cooling rate and therefore the latter determines the rheological properties of oil. It is reasonable to suppose that the slower the cooling, the higher the degree of crystallinity and the higher the viscosity. However in reality the opposite is true: the viscosity of oil decreases when the cooling rate slows down. In this work, a model explaining this unexpected effect is proposed. The model is based on the relationship between the cooling rate and the temperature at which the viscosity increases unlimitedly.

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1. Introduction

In flow (or in pipe transportation) of crude waxy oils as well as oil-based emulsions, numerous effects takes place due to the temperature-dependent crystallization of paraffins in the working temperature range. So, the kinetics of the phase transition is superimposed on the flow, leading to changes in the rheological properties of the oil over time. If the paraffin concentration exceeds some threshold, it creates some special structure. Then the oil becomes a visco-plastic medium characterized by some yield stress. It is known that even 4% paraffin (or maybe even less) is sufficient for the appearance of all characteristic effects due to its crystallization [1–3], while the content of paraffin in industrial oils reaches 20–24%.

Structural effects related to paraffin crystallization occur in the definite temperature range between the melting point T_m (wax appearance temperature—WAT, or cloud point) and temperature of the loss of fluidity (pour point), T_p . It is important that T_m depends weakly on the cooling rate ([4], Fig. 4) and could be treated as the material constant of oil. However, as demonstrated for model systems, T_m depends on the content of crystallizable components [5].

The interval $\Delta = T_m - T_p$ is the main interest for quantitative understanding of the evolution of the rheological properties during cooling. It is worth noting that the effects under discussion are

observed not only in crude oil but also in oil-based emulsions in which crystallizable components are present. In the temperature range above T_m , oil can be treated well as a Newtonian fluid whose viscosity depends only on temperature (see e.g., [6]). Certainly, oils which are Newtonian fluids over the whole of a wide temperature range also exist. For example, this is true for some sorts of Norwegian heavy oils [7]. However in general, oil and especially waxy oil should be treated as a structuring medium. The kinetics of structuring in waxy oils is determined by temperature. It is well known that the rheological properties of waxy oils and viscosity, η , in particular, depend on the cooling rate [4,8]. This phenomenon is explained by the crystallization of paraffin (and some other) fractions. However, paradoxically, it appears that the lower the rate of cooling (which promotes crystallization), the lower the viscosity of oil. This phenomenon is clearly seen from experimental data of the publications [4] (Figs. 7, 8, 11, 12) and [8] (Fig. 9).

In this work, this effect is discussed and explained on the basis of a proposed model which quantitatively describes the dependence of the viscosity of waxy oils on the cooling rate. At the chosen approximation, the viscosity is treated as Newtonian and the yielding effect is not considered.

2. Model

Let us first consider the two limiting situations. In the first case, very rapid cooling takes place. In this case, crystallization is excluded and the viscosity grows unlimitedly when approaching some temperature, T_p . In the second case, very slow cooling occurs and complete crystallization occurs in all those oil components

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which are able to crystallize. Their concentration is φ^* , and after crystallization, they separate from the mass of the fluid. The non-crystallized part of the matter remains fluid in the whole temperature range. The crystals play the role of a solid filler. In all intermediate cases, crystallization occurs to some degree φ less than the limiting value φ^* .

So, the simplest possible model of oil as a two-component system is considered. In reality, oil is a multi-component system with rather complicated composition, where all components with different molecular weights, branching, cyclizing, and so on give their own contribution to the viscosity. However in the frames of a qualitative model these factors play a secondary role and do not affect the physical scenario.

The content of the proposed model consists of the following steps:

- Determination of the dependence of the degree of crystallinity, φ , on the cooling rate, w .
- Determination of the dependence of the oil viscosity, η , on the degree of crystallinity, φ , and the cooling rate, w .

So, it is assumed that there are two co-existing states of the matter: a fluid which can pass to a non-fluid state and a fluid containing some amount of solid particles (paraffin crystals). For simplicity, we will assume that the temperature dependence of viscosity of both is characterized by the same coefficient U .

The temperature dependence of the viscosity of a solidifying fluid is described by the Vogel–Fulcher–Tammann-type equation:

$$\eta = \eta_0 e^{U/R(T-T_p)} \quad (1)$$

The temperature dependence of a fluid with the solid filler is described by the Arrhenius equation:

$$\eta = \eta_0 e^{U/RT} f(\varphi) \quad (2)$$

Here, $f(\varphi)$ is a function presenting the influence of a solid filler on the viscosity of a fluid containing crystals. As a rule, φ does not exceed 0.2–0.25. Thus this function (for suspensions) can be presented by a well-known quadratic polynomial [9]:

$$f(\varphi) = 1 + 2.5\varphi + 5.0\varphi^2 \quad (3)$$

The central part of the modeling is finding the dependence of the degree of crystallinity on the cooling rate, $\varphi(w)$. To do this, it is necessary to use the kinetic equation for the rate of crystallization. It should be noted here that it would be rather inconvenient to use the Avrami type equation or any other equation for the isothermal crystallization based on the $\varphi(t)$ function because such equations are rather awkward for integration with respect to temperature. As shown in [10], the problems of the non-isothermal kinetics can be much more conveniently solved using kinetic equations of the differential type, for example the following one:

$$\frac{d\varphi}{dt} = A(1-\varphi)(1+K\varphi) \quad (4)$$

The temperature-dependent parameter in this equation is A , which can be written as:

$$A(T) = A_0 e^{E/R(T-T_p)} \quad (5)$$

In this equation, K is the factor of self-acceleration, E is the temperature coefficient of the crystallization rate, and A_0 is the usual pre-exponential factor.

The introduction of the difference $(T - T_p)$ in the denominator of the exponent shows that the crystallization process decelerates in approaching $T \rightarrow T_p$ and stops at T_p .

Generally speaking, the temperature dependence of the crystallization rate has a bell-like shape and the rate tends to zero in

approaching to the glass transition temperature. The glass transition temperature of paraffins lies much below zero Celcium. Here only a narrow temperature range close to the melting point is discussed. So, it seems reasonable to treat the rate dependence as monotonous (Eq. (5)).

It is worth mentioning that Eq. (4) for the isothermal process is practically identical to the one described by the Avrami equation, but it is better to adopt Eq. (4) for analysis of any non-isothermal processes.

The integral form of Eq. (4) has the form:

$$A_0 \int_0^{t_{cr}} e^{-E/R(\Delta-wt)} dt = \int_0^{\varphi} \frac{d\varphi}{(1-\varphi)(1+K\varphi)} \quad (6)$$

where, the upper limit of the left-side integral, t_{cr} , is the duration of the crystallization process, which is equal to the temperature interval of crystallization, Δ , divided by the crystallization rate w .

$$t_{cr} = \frac{T_m - T_p}{w} = \frac{\Delta}{w} \quad (7)$$

After some rearrangements, the left-side of Eq. (6) can be written as $A_1 \Delta/w$ and the right-side is $\frac{1}{1+K} \ln \frac{1+K\varphi}{1-\varphi}$, where, A_1 combines several constants used above. Then the following equation for calculating φ has been obtained:

$$\frac{A_1 \Delta}{w} = \frac{1}{1+K} \ln \frac{1+K\varphi}{1-\varphi} \quad (8)$$

Finally, the solution obtained is:

$$\varphi = \frac{e^{D/w} - 1}{e^{D/w} + K} \quad (9)$$

where,

$$D = A_1 \Delta (1 + K) = \text{const.}$$

D has the meaning of the characteristic rate constant of the crystallization process.

Assuming that the constant K is large in comparison with $e^{D/w}$ (φ would always be of the order of unity in the opposite case), the following final formula has been obtained:

$$\varphi = \frac{e^{D/w}}{K} \quad (10)$$

It is evident that the value of φ decreases sharply (exponentially) along with an increase in the cooling rate. If the cooling rate is low then $e^{D/w} \gg K$ and Eq. (9) shows that the maximal possible degree of crystallinity $\varphi^* = 1$ is reached.

It is important to stress that the final results of calculations, Eqs. (9) and (10), are valid not only for cooling the waxy oil but also for a variety of situations in which incomplete crystallization takes place, for example, for technological processes when quick cooling occurs.

So, Eqs. (9) and (10) present the solution of the first task—finding the degree of crystallinity φ on cooling as a function of the cooling rate w .

Now let us turn to the estimation of the changes in viscosity at the maximal possible degree of crystallinity φ^* . As the reference point, the viscosity value at temperature T_m was taken. Then the following expression based on Eq. (2) can be written as

$$\eta(T_p) / \eta(T_m) = e^{U/RT_p} f(\varphi) / e^{E/RT_m} = e^{\frac{U\Delta}{RT_p T_m}} f(\varphi) \quad (11)$$

Now the intermediate cases of incomplete crystallization should be considered. The degree of crystallinity is calculated from Eq. (10). The following assumption is important for the further argumentation. Let us assume that a decrease in the share of crystallizable components leads to a shift of the temperature T_p , which decreases

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