

## INVESTIGATIONS ON THE RHEOLOGY OF WATER-IN-CRUIDE OIL EMULSIONS

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*Lucrarea este dedicată cercetărilor experimentale și modelării reologice ale emulsiilor de apă în țigări. Probele utilizate în experimente au la bază două feluri de țigări românești: proba PA, un țigări asfaltic cu o concentrație volumică de apă de 30% și, respectiv proba PB, un țigări parafinic cu concentrație volumică de 6% apă. În vederea caracterizării reologice (dependența viscozității și elasticității de viteza de deformare, respectiv de frecvența de oscilație) cele două probe au fost supuse la teste de forfecare și teste oscilatorii la temperatură de 5°C. Testele mai sus menționate au pus în evidență diferențe importante ale proprietăților de curgere între cele două probe. În urma studiului realizat asupra emulsie parafinoase s-a propus o relație constitutivă capabilă să modeleze caracterul său tixotropic și existenței pragului de curgere.*

*The paper is concerned with the experimental investigations and rheological modelling of water-in-oil emulsions. The probes used in experiments are based on two Romanian crude (pure) oils: probe PA is an asphaltic crude oil with 30% water volumic concentration, and probe PB is a paraffinic crude oil with 6% water volumic concentration. Simple shear and oscillatory tests have been performed at temperature of 5°C in order to characterise the rheology of the samples (i.e. dependences of viscosity and elasticity on the shear rate, respectively on the frequency) and to evidence the differences between their flow properties. The study is focused to the paraffin based emulsion and a constitutive relation with unstable flow curve is proposed to model the sample's complex (thixotropy and yield stress) rheological behaviour.*

**Keywords:** Rheology; Oil-water emulsion; Paraffinic oil; Viscoelasticity; Shearing flow; Oscillatory test; Thixotropy.

### 1. Introduction

Oil-water emulsions are viscoelastic fluids which disclose a complex rheology, shear thinning behavior and thixotropic effects being observed in most of the samples beyond a critical water concentration and below a threshold temperature, for details see Aomari et al. [1], Farah et al. [2], Johnsen and Rønning [3]. The corresponding flow properties of these fluids, as viscosity

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and elasticity at constant water concentration, temperature and pressure, are determined by two factors: (i) the composition of the base crude oil (Aske, [4]) and, (ii) the interfacial tension between oil and water (Langevin, [5]). In practical applications, the rheological properties are mainly related with the control and optimization of oil-water flows in pipes; minimization of the energy loss during the transport (Naseri et al., [6]; Vinay et al., [7]) and formulation of proper polymers additives as surfactants for oil-water emulsions (Al-Roomi et al., [8]; Broboana et al., [9]) being the main goals of researches. An extensive literature has been published on the experimental rheology of oil-water emulsion, but only few papers were dedicated to the rheological modeling of the samples.

The present paper is concerned with the rheological investigations and modeling of water-in-oil emulsions based on two Romanian crude (pure) oils: probe A (PA) is an asphaltic crude oil with 30% water volumic concentration and probe B (PB) is a paraffinic crude oil with 6% water volumic concentration. In the absence of any surfactant and at constant water concentration, temperature is the main parameter which make the difference on the samples rheology.

The work is focused to the rheological investigations of water-in-paraffinic oil emulsion (PB) at temperature of  $\theta_0 = 5^\circ \text{C}$ . The test temperature is between the “cloud point” temperature,  $\theta_c \approx 16^\circ \text{C}$  (considered as WAT – wax appearance temperature), and the pour point  $\theta_p = 4^\circ \text{C}$  (at normal pressure). The goal of the experimental investigation is to evidence the main anomalous rheological effects induced by the wax network within the liquid, respectively thixotropy and time dependence of the flow curve under controlled shear rate tests.

It is well known that paraffin molecules precipitate in solution at temperature lower than WAT (Webber, [10]; Garcia et al., [11]; Venkatesan et al., [12]). As temperature is decreasing, the wax crystals are formed, deposit and finally paraffin crystals are organized in a network structure. At pour point and below the paraffinic crude oil is transforming in a gel which deposit at the solid walls of the pipes and reduce drastically the flow area (Coutinho et al., [13]; Seth and Towler, [14]). Therefore understanding and modeling the rheology of paraffin oil at low temperatures is of great interest. One aim of our study is to relate the rheological experimental data of water-in-paraffinic oil emulsion with a family of constitutive relation. The experiments in viscometric motion disclose shear rate dependence of viscosity function, respectively coexisting of thickening and thinning behaviours in a same flow curve and thixotropic effects, corroborated with elasto-plastic effects.

This complex rheology is qualitatively described by the intrinsic unstable constitutive model, an extension of the Johnson and Segalman relation presented by Balan and Fosdick [15] and Balan [16].

## 2. Experimental

Rheological characterisations of the emulsions (samples PA and PB) and the based crude oils are obtained at temperature of 5° C and normal pressure. Oscillatory, stressing and creeping tests have been performed in order to characterise the rheology of the probes (i.e. dependences of viscosity and elasticity on the oscillatory frequency, respectively shear rate) using MC 300 and MC 1 Physica rheometers. The geometry for the tests were cone and plate (oscillatory tests on MC 300), double Couette geometry, for creeping and stressing tests on MC 1, respectively.

In Fig. 1 and Fig. 2 are presented the experimental results for PA and the asphaltic based crude oil-A, and in Fig. 3 and Fig. 4 are shown the corresponding experimental data for PB and the paraffinic based oil-B.

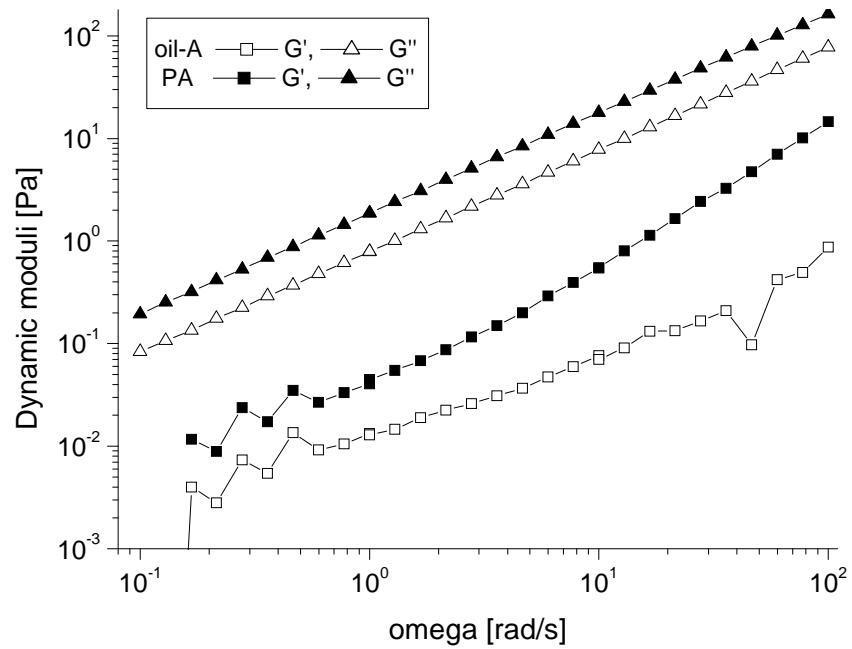


Fig. 1. Elastic and loss moduli for crude oil-A and probe PA.

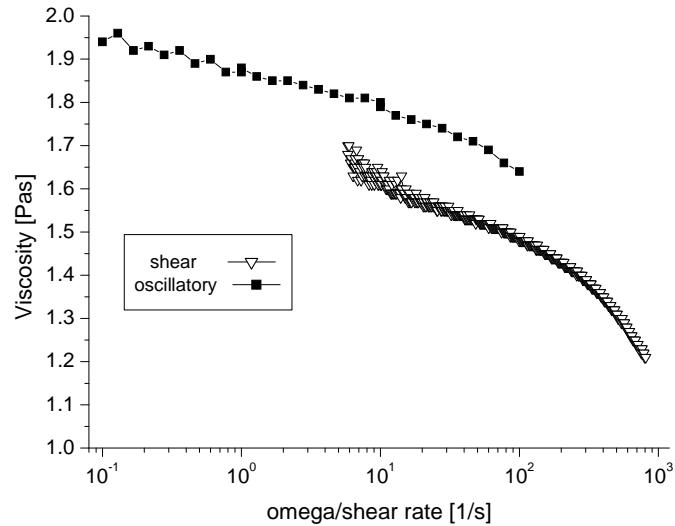


Fig. 2. Complex and shear viscosity for probe PA (controlled shear rate test:  $1\text{ s}^{-1}$  to  $1000\text{ s}^{-1}$  in  $1000\text{ s}$ ; 100 measured points, 5 s/point).

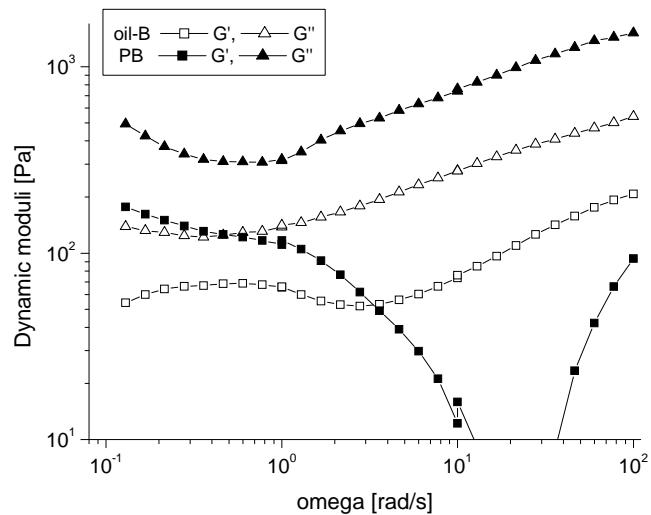


Fig. 3. Elastic and loss moduli for crude oil-B and probe PB.

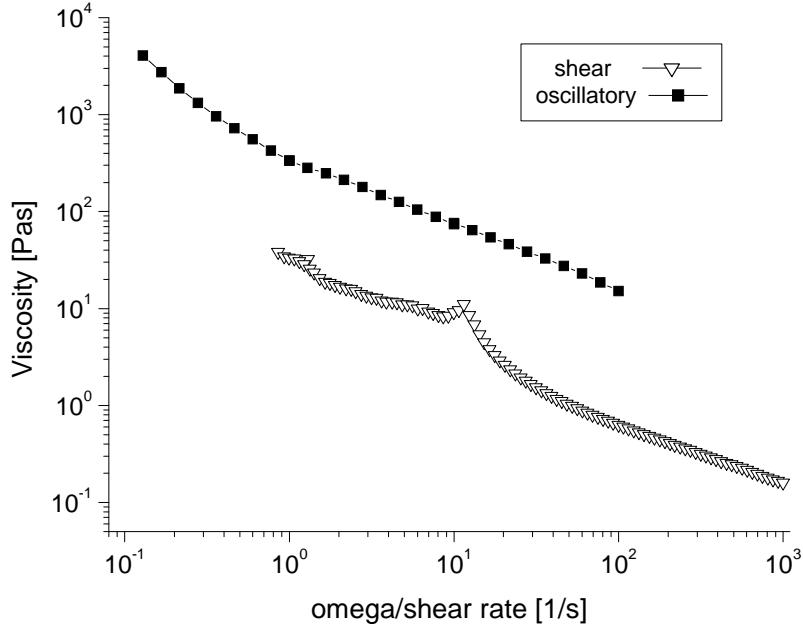


Fig. 4. Complex and shear viscosity for probe PB (controlled shear rate test:  $1\text{ s}^{-1}$  to  $1000\text{ s}^{-1}$  in  $1000\text{ s}$ ; 100 measured points, 5 s/point).

Emulsions are viscoelastic fluids for which complex viscosity is higher than shear viscosity, see Fig. 2 and Fig. 4, also Aomari et al. [1] and Broboana et al. [9]. Both samples disclose a shear thinning character, more relevant for PB due to fragility of the paraffin bonds.

Comparison between the oscillatory tests for PA and PB, see Fig. 1 and Fig. 3, put in evidence the qualitative and quantitative differences between samples. The values of viscosity and elasticity for PA are representative for weakly elastic high viscous liquids, whereas the values measured for probe PB define the existence of a gel structure.

The emulsion PA discloses higher values of rheological properties than the asphaltic based crude oil and a usual frequency dependence of the elastic modulus,  $G'(\omega)$ , and viscous modulus,  $G''(\omega)$ , for a viscoelastic non-linear liquid (Macosko [17]). The shear thinning character is observed in Fig. 2, but is not quantitative relevant. Elasticity is present in simple shear, but the magnitude of elastic modulus is small,  $G' < 1\text{ Pa}$  for  $\omega < 100\text{ s}^{-1}$ .

Rheology of PB and corresponding crude oil is dominated by the answer of paraffin network within the viscous oil (Fig. 3 and Fig. 4). The plateau

behaviour for the moduli at low frequencies suggest a gel like structure (see also Singh et al. [18]). The decrease of  $G'(\omega)$  with increasing frequency for PB in Fig. 3 is generated by the fragile character of the paraffine network structure within the emulsion at high frequencies.

In Fig. 4 the shear viscosity of PB discloses a local maximum at medium shear rate and a significant “global” shear thinning behaviour. The non-monotonous dependence of viscosity function  $\eta(\dot{\gamma})$  is an indication that PB might disclose a more complex rheological character (we are referring here to thixotropy). Thixotropy is a time dependent rheological behavior determined by the change of molecular structure due to shearing. Thixotropy is relevant if the flow curve and viscosity function disclose also dependence on the shear stress gradient, not only on the level of shear rate. In Fig. 5 are shown the results of a thixotropic test applied to PB sample: shear rate is increasing from  $1 \text{ s}^{-1}$  to  $1000 \text{ s}^{-1}$  and decreasing back to  $1 \text{ s}^{-1}$  in  $1000 \text{ s}$  (100 measured points, 5 s/point). The results disclose two remarkable thixotropic effects: (i) local thickening of the “up” flow curve at medium shear rate, and (ii) relevant difference between the “up” and “down” flow curves (same test applied to the probe PA produces monotonic flow curves and identical “up” and “down” measured points, see Broboana et al., [9]).

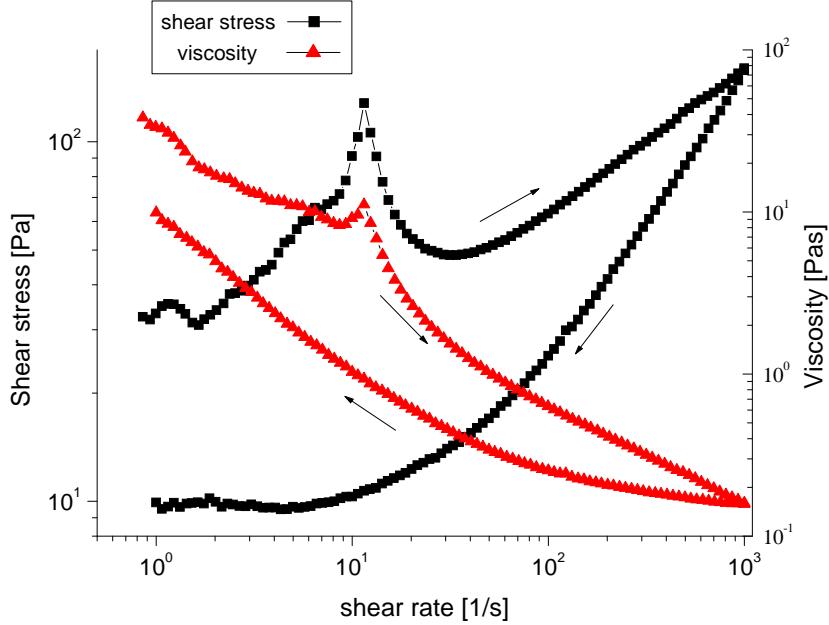


Fig. 5. Thixotropy test for probe PB.

The experimental investigations of the two emulsions at low temperature put in evidence the complex rheology of probe PB, in comparison to the asphaltic oil based probe. Of course, the difference is made by the paraffin precipitation below WAT, which create an unstable structure within the fluid (Singh et al., [18]; Venkatesan et al., [12]).

The probe PA behaves as a viscous fluid enriched with particles; no remarkable elasticity, weak shear thinning effects and lack of thixotropy are observed. In Broboana et al. [9] is shown that viscosity function of the water-in-asphaltic oil emulsions can be fair modeled with the Carreau-Yasuda relation, for a large range of temperature and different surfactants concentrations.

The present paper is focused to the shear rheology investigations of the water-in-paraffinic oil emulsion at low temperature, where the wax structure is present. In the next paragraph the thixotropic behaviour of the PB probe is analyzed in more details and a constitutive relation for the sample is proposed. In particular, at this stage of research, the authors are interested to establish the rheological model able to represent properly the observed thixotropic effects of the sample.

### 3. Rheological modeling

The non-monotony of the flow curve and thixotropy, associated with the viscoelastic behavior, make from PB one of the most difficult fluid to be modeled from the rheological point of view. Actually, there are no constitutive relations able to represent, both from qualitative and quantitative point of view, all these macroscopic flow characteristics.

To have a more general picture of PB sample, we performed additional tests, some of them being presented in Fig. 6 and Fig. 7, respectively Fig. 8.

In Fig. 6 has been investigated the influence of the shear history on the flow curve. There are represented four curves obtained at different test conditions, i.e. different slopes in time for the increasing of the shear rate –  $\dot{\gamma}$  in the interval  $[1, 1000] \text{ s}^{-1}$  (the experimental time for each measured point is different, from 1 s to 2000 s). The test procedure assumed an identical thermal history for all measurements. Each test was performed with new sample and before test the samples were mixed at low velocity and constant temperature of  $5^\circ \text{C}$  for 5 minute (the influences of thermal and shear history on wax oil rheology is presented by Singh et al. [18]). In Fig. 7 the corresponding viscosity functions are displayed.

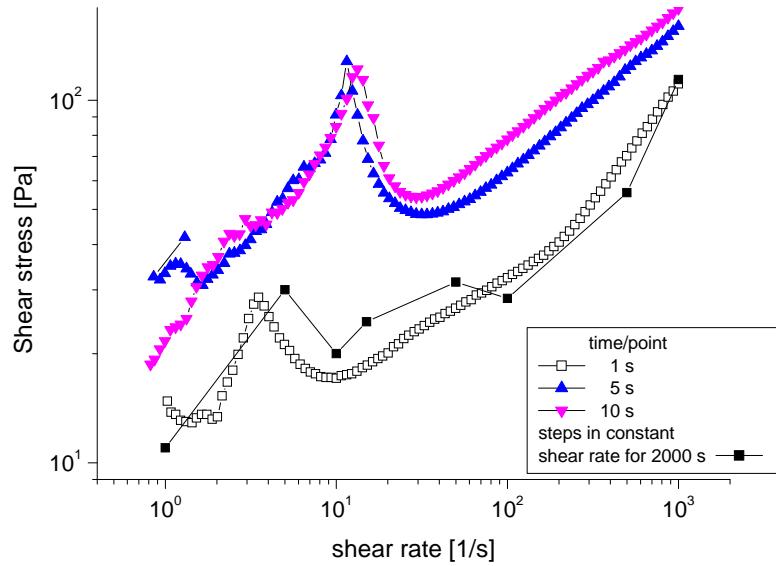


Fig. 6. Dependence of flow curve on the input data for probe PB.

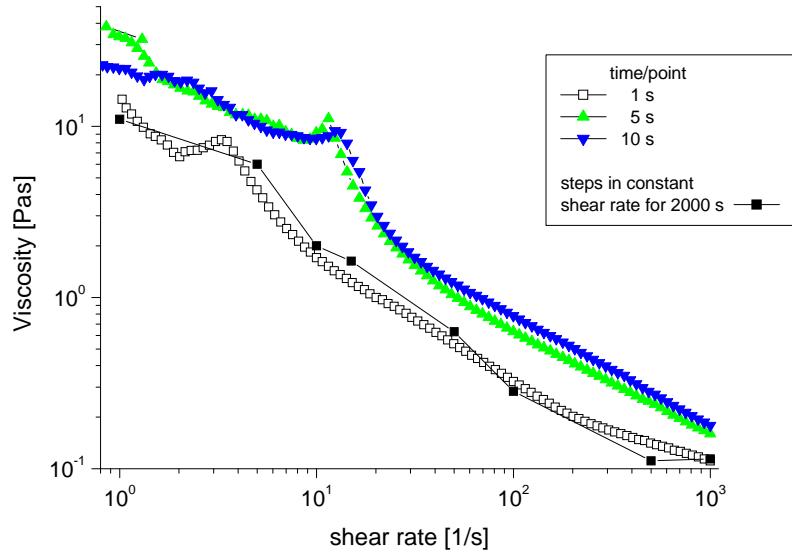


Fig. 7. Dependence of shear viscosity on the input data for probe PB.

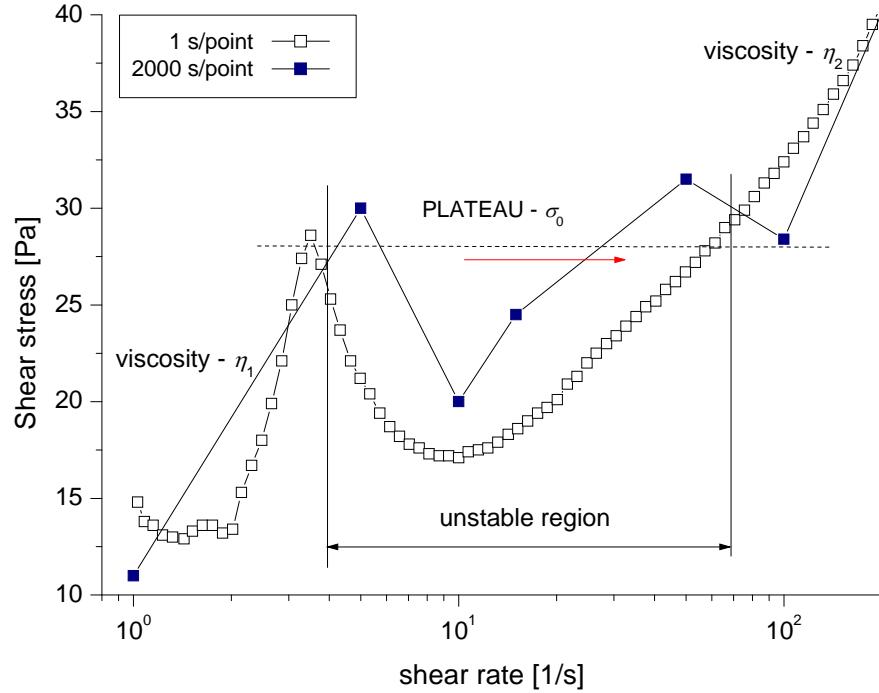


Fig. 8. Transitory and “steady” flow curve for PB (detail).

It is important to remark that flow curve has the tendency to reach asymptotically a steady state “plateau” in the range  $\dot{\gamma} \in (3, 100) \text{ s}^{-1}$ , see Fig. 8. The observed flow behavior suggests that PB might be properly described by a family of constitutive relation with non-monotonous flow curves, i.e. viscoelastic models with intrinsic material instability. This rheological behaviour has been also remarked for lubricating greases, where the lithium network structure is embedded in a mineral oil, for details see Balan [19], Balan and Franco [20].

The experiments from Fig. 8 disclose an “unstable region”, i.e. a plateau in steady flow curve corresponding to a constant shear stress  $\sigma_0$ , between two regions with high, respectively low viscosity ( $\eta_1 >> \eta_2$ ). We have also to remark that steady state (if exists!) is obtained after a long time of shearing, due to the persistent influences of the shear and thermal histories on the rheology of the sample.

The jump in shear rate is characteristic to the banding flow structure within the gap of rheometer. In this type of flow, two or more layers of constant

shear rate are moving under a constant applied shear stress. The phenomena was observed and investigated for the wax-oil samples by Singh et al. [18].

One can conclude that local thickening is a non-stationary rheological behaviour associated to the plateau onset of the steady flow curve, therefore to an unstable constitutive relation. In Fig. 9 is shown the results from a transitory shear rate controlled test which proves the thixotropy of the probe PB. Two steps for 60 s of constant shear rate (values of  $1 \text{ s}^{-1}$ ,  $10 \text{ s}^{-1}$ ,  $100 \text{ s}^{-1}$  and  $500 \text{ s}^{-1}$ , respectively) are applied, with no shear between (fluid at rest for 60 s), followed by a shear of 150 s. This test reveals remarkable transitory effects, the rebound of the wax structure after shear (remarkable at  $\dot{\gamma} < 100 \text{ s}^{-1}$ ) and the shear history (time) dependence of the process (the rebound magnitude is decreasing in time,  $a_2 < a_1$  at  $\dot{\gamma} = 10 \text{ s}^{-1}$ , see Fig. 9). At low shear rate ( $\dot{\gamma} = 1 \text{ s}^{-1}$ ) the phenomena is accentuated and corroborated with the presence of shear stress oscillations, due to dynamics of the unstable network structure. Beyond  $\dot{\gamma} = 100 \text{ s}^{-1}$  the internal network structure is destroyed and all the mentioned effects are no more relevant for samples rheology (for that reason the “down” flow curve represents a typical viscous fluid behavior, see Fig. 5).

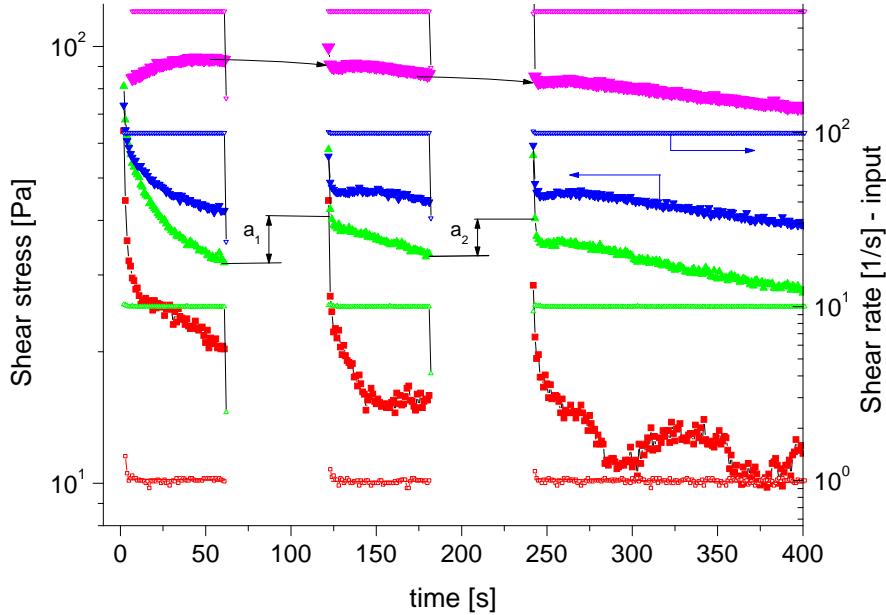


Fig. 9. Time dependence of shear stress at constant rate for probe PB.

The proposed unstable constitutive relation is presented in details by Balan [15, 19, 20]; it is a modified Johnson and Segalman model characterized by a non-monotonic flow curve, see Fig. 10.

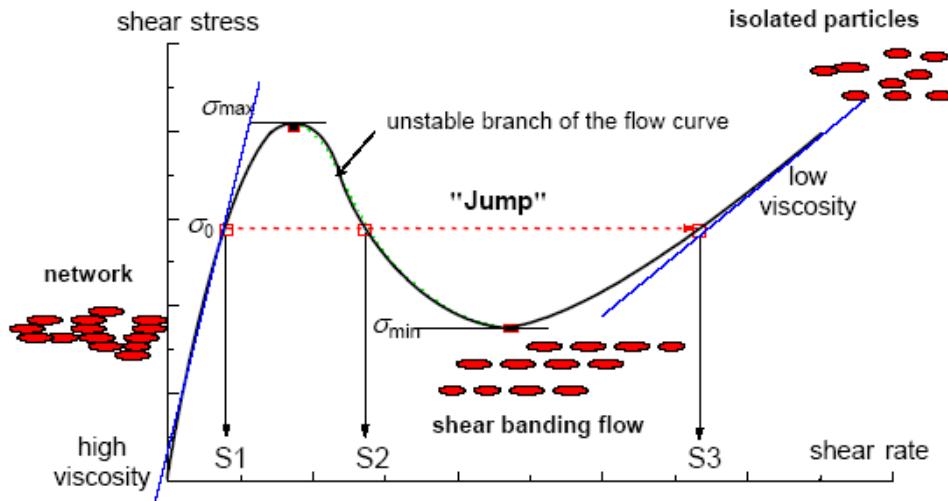


Fig. 10. Representation of non-monotonic flow curve

The differential constitutive relation which discloses a non-monotonic behaviour in simple shear flow is,

$$\lambda_1 \frac{D_1 \mathbf{T}}{Dt} + \mathbf{T} = 2\eta_0 \lambda_2 \frac{D_2 \mathbf{D}}{Dt} + 2\eta_0 \mathbf{D}, \quad (1)$$

where  $\mathbf{T}$  is the extra-stress,  $\mathbf{D}$  and  $\mathbf{\Omega}$  are the stretching and the spin tensors, respectively.

In (1)  $D_i \cdot / D_i t = d \cdot / dt - \mathbf{\Omega} \cdot + \cdot \mathbf{\Omega} - a_i (\mathbf{D} \cdot + \cdot \mathbf{D})$  is the general Gordon-Schowalter objective time derivatives, the symbol  $d \cdot / dt$  being the material time derivative. Relation (1) is dependent on five parameters: the material constants  $\lambda_1, \lambda_2$  and  $\eta_0$  (time of relaxation, time of retardation and zero shear viscosity) and the “slipping parameters”,  $a_1, a_2 \in [-1, 1]$ , which define the type of objective derivatives for the extra stress and for the stretching, respectively. The convected derivatives are defined for  $a_{1,2} = \pm 1$  and  $a_{1,2} = 0$  defines the Jaumann (corotational) derivative; in the original Johnson and Segalman model was used a single slipping parameter,  $a = a_1 = a_2 \neq \pm 1$ .

The corresponding expression for the steady shear stress  $\sigma$  in a viscometric flow is given by

$$\sigma = \eta_0 \dot{\gamma} \frac{1 + \kappa \lambda_1^2 \dot{\gamma}^2}{1 + \lambda_1^2 \dot{\gamma}^2} \quad (2)$$

where  $\kappa = \lambda_2 / \lambda_1$  and  $a_{1,2} = 0$ . From (2) the viscosity function can be computed easily with formula

$$\eta(|\dot{\gamma}|) = \frac{\sigma}{\dot{\gamma}}. \quad (3)$$

A real material is usually fitted with a series of “ $n$ ” elements (1) connected in parallel, i.e.  $\mathbf{T} = \sum_{i=1}^n \mathbf{T}_i$  and  $\sigma = \sum_{i=1}^n \sigma_i$ , each of the extra-stress  $\mathbf{T}_i$  being given by (1), respectively (2).

The results of fitting for two elements ( $n = 2$ ) are shown in Fig. 11 and Fig. 12, where there were used the following values for the material constants in (2):  $\eta_{01} = 10$  Pas,  $\eta_{02} = 1$  Pas;  $\lambda_{11} = 0.2$  s,  $\lambda_{12} = 0.02$  s and  $\kappa = 0.01$  for both elements.

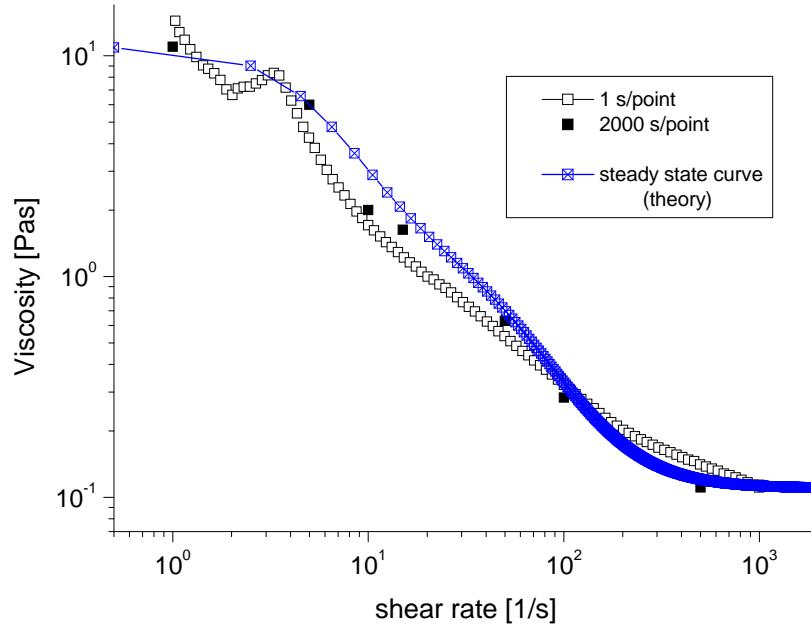


Fig. 11. Theoretical steady viscosity function and experimental data from Fig. 7.

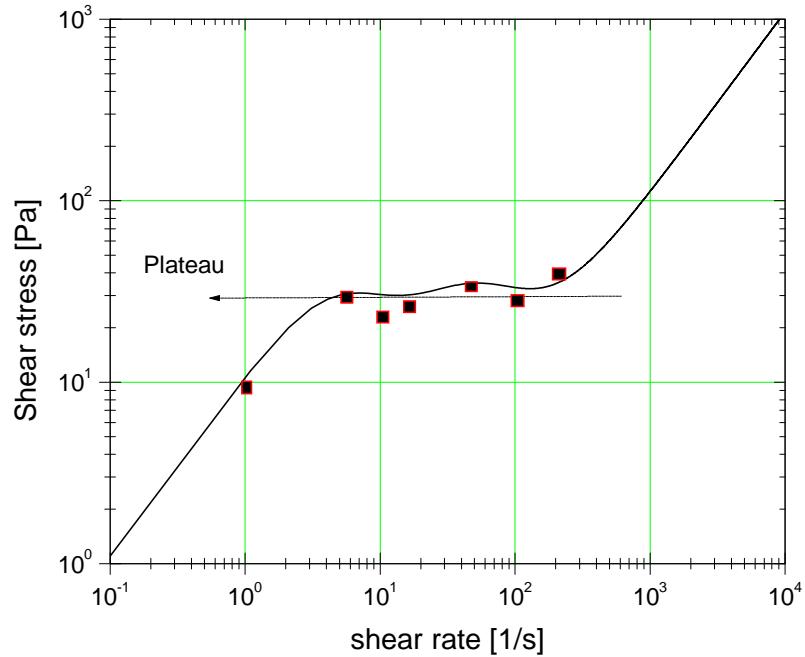


Fig. 12. Theoretical steady flow curve and the experimental “steady data” from Fig. 8.

The results from Fig. 11 and Fig. 12 prove the capabilities of model (1) to offer a fair representation of the emulsions rheology.

The associated dynamics of the proposed model is consistent with the experimental data presented in this paper, also with the visualizations performed by Singh et al. [18] and numerical simulation of Bingham model from Vinay et al. [7]. The corresponding velocity distribution in a simple shear flow is given in Fig. 13. The shear at constant stress  $\sigma_0$ , see Fig. 10 and Fig. 12, and constant first normal stresses differences  $N_1$  produces a multiple layers structure. One possible flow pattern is the existence, in the very vicinity of one wall, of a layer of thickness  $\delta$  with low viscosity and high shear rate (solution S3) and a domain characterized by high viscosity, which corresponds to low shear rate (solution S1). The separation, i.e. the plateau, is a “kink” in the velocity distribution, respectively a point of discontinuity in the first derivative of velocity.

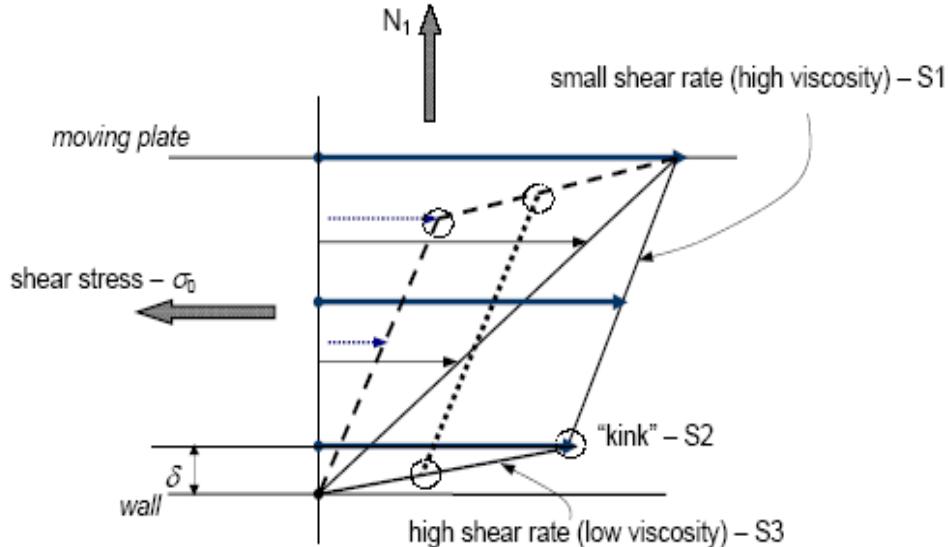


Fig. 11. Possible velocity distributions in a simple shear motion of an unstable constitutive relation, see also Fig. 10.

Solution S1 corresponds to the “gel” phase of the sample (i.e. wax network structure), whereas solution S3 define the “liquid layer”. The crucial role in establishing the flow pattern in simple shear has the answer of wax network, respectively the initial values of  $N_1$  coefficient at the onset of shearing.

#### 4. Conclusions

The paper present the experimental investigations and modeling of the rheological behavior of emulsions in simple shear and oscillatory viscometric flows, at low temperatures. The fluids under investigation are water-in-oil emulsions based on two different Romanian crude oils: (i) asphaltic oil – probe PA, and (ii) paraffinic oil – probe PB. The research is focused to the study of probe PB, sample which discloses a relevant thixotropic character due to wax precipitation.

The performed experiments are consistent with the previous data published in literature and evidence the instability of the paraffin network structure in shearing, at temperatures between WAT and pour point. Thixotropy, local thickening of non-stationary flow curve and stress oscillations under constant shear rates are important experimental results which indicate the suitable constitutive family for the water-in-paraffinic oil emulsions.

The paper proposes a constitutive relation for the tested probe PB based on the unstable Johnson and Segalman differential model, which discloses a non-monotonic steady flow curve and a dynamics sensitive to initial conditions. The model is consistent to the experimental evidences of sample phase separation in the gap of the rheometer, also with the plateau existence in the steady flow curve and transitory thickening of viscosity function.

The obtained experimental data in shearing and the constitutive modelling are qualitatively consistent. The results are very promising for the further applications of our study; we are here referring to the optimization of the flow emulsions in pipes, respectively to the modelling of emulsions rheology in the presence of surfactants.

The correlation of rheological properties with the flow regime, in order to minimize the energy for the oil transport in pipes, represents one of the major scientific target of today applied fluid mechanics. The present study is a premiere in Romania; it is a first step in understanding of a complex scientific problem with a very positive economical impact. The present experimental studies and modelling bring a better understanding of flow properties of Romanian oils and have a direct application in optimization of oil transport in pipes.

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