STUDIA UBB CHEMIA, LVI, 3, 2011 (p. 247 – 255)

THE RHEOLOGICAL STUDY OF SOME SOLUTIONS BASED ON SURFACE-ACTIVE AGENTS (II)

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ABSTRACT. The paper presents the rheological behavior study of some solutions based on surface-active agents used as auxiliaries in oil extraction technology. The influence of surfactants' structure and concentration was determined, as well as that of temperature, on the rheological behavior, by setting the dependence between the shear stress τ and the shear rate $\dot{\gamma}$. The analysis of dependence $\tau = f(\dot{\gamma})$ demonstrates that the solutions studied present non-Newtonian behavior (yield-pseudoplastic and simple pseudoplastic).

Keywords: *Yield-pseudoplastic behavior, shear rate, shear stress, surfactant*

INTRODUCTION

In the oil extraction process, after a certain period of operation, oil-wells depletion occurs, that means a drasting drop in productivity. The phenomenon is mostly significant in the case of the deposits whose structure is based on clays [1]. In order to increase the layer porosity and permeability, a porous material (usually sand of a certain granulation) is introduced in the deposit through the existing cracks. The sand spreading must be done by means of a fluid carrier. The first types of fluid carriers were hydrogels (hydroxyethyl-cellulose, carboxymethylcellulose). Subsequently, viscoelastic solutions (with cationic surfactants content) were used. Surfactant molecules in solution can self-assemble into aggregates (micelles). The shape and size of micelle depend on the molecular structure of the surfactant, nature of solvent and additives and their molar composition.

Wormlike micelles are large one-dimensional aggregates and behave like a semi-flexible polymeric chain. Their rheological properties in aqueous solutions have a remarkable resemblance to those of polymers in a good solvent [1]. The addition of inorganic salts decreases the electrostatic interactions between monomers in the micelle, which induces micellar growth and viscosity increment [1].

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The main characteristics of the surface-active agents (A, B, VB, VAD) are found in Table 1, and the composition of the solutions with A and B content is presented in Table 2. The composition of the solutions with VAD and VB content can be expressed as PA_{i-j}, where i is the wt % of VAD and j is the wt % of VB (For example: $PA_{3\text{-}9}$ contains 3%VAD+9% VB + 88% water).

Table 1. The properties of the surface-active agents used

Symbol	**Type**	**Active substance %**	**Molecular weight,** $kg \cdot kmol^{-1}$	**pH of 1% aq. solution**
VB	amphiphilic	30	355	7÷7.5
VAD	weakly cationic	100	488	-
A	cationic (alkyl trimethyl NH^{+}_{4} chloride)	30	263	-
B	aromatic carboxylic acid (Na salt)	40	180	-

Table 2. The composition of solutions with A and B content

Symbol	**Composition, wt %**
PC_1	1% B + 99% sol.1*
PC_2	2% B + 98% sol.1*
PC_3	3% B + 97% sol.1*
PC_4	4% B + 96% sol.1*
PC_5	5% B + 95% sol.1*

***** The composition of sol. 1 is (wt %): 88.24% water + 9.8% A + 1.96% NaCl.

The preparation of solutions was done by dispersing water under intense stirring in surfactants mixture (VAD+VB and A+B, respectively) at room temperature (t~25°C).

The rheological characterization of the solutions prepared was carried out using rotational viscometer Rheotest-2, under thermostatic conditions. It was followed the establishment of rheological relations $\tau = f(\dot{\gamma})$ where τ and $\dot{\gamma}$ are the shear stress and the shear rate, respectively, as well as the calculation of the activation energy of viscous flow E_a.

The characterization of liquids flow in ring-shaped spaces is expressed using the Taylor-Reynolds number, Ta_{Re} which depends on the geometry of the ring-shaped space (radii of the two cylinders, r_o, r_i), shear rate $\dot{\gamma}$ or revolution n, liquid density ρ and apparent viscosity η_a [2]:

$$Ta_{\mathrm{Re}} = \frac{2 \cdot \pi \cdot n \cdot \left(r_o^2 - r_i^2\right) \cdot \rho}{\eta_a} \qquad (1)$$

$$\dot{\gamma} = \frac{2 \cdot \pi \cdot n \cdot r_o^2}{r_o^2 - r_i^2} \qquad (2)$$

RESULTS AND DISCUSSION

1. The temperature influence

The influence of temperature on the rheological behavior was determined for samples $PA_{2\text{-}8}$, $PA_{2.5\text{-}8}$, and the series PC_1-PC_5. In Figure 1, dependence $\tau = f(\dot{\gamma})$ is shown, at different temperature values, for $PA_{2.5\text{-}8}$.

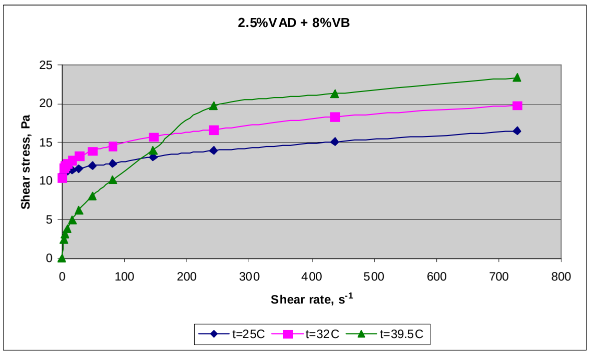

Figure 1. Dependence $\tau = f(\dot{\gamma})$ for $PA_{2.5\text{-}8}$ at different temperatures

The rheological equations for samples $PA_{2\text{-}8}$ and $PA_{2.5\text{-}8}$ are presented in Tables 3 and 4.

Table 3. Rheological equations for $PA_{2\text{-}8}$ sample at various temperatures

Temperature, ºC	Equation
32	$\tau = 13.9 + 0.78 \cdot \dot{\gamma}^{0.263}$
39.5	$\tau = 12.8 + 0.47 \cdot \dot{\gamma}^{0.553}$

Table 4. Rheological equations for $PA_{2.5\text{-}8}$ sample at various temperatures

Temperature, ºC	Equation
25	$\tau = 10.8 + 0.13 \cdot \dot{\gamma}^{0.575}$
32	$\tau = 10.4 + 0.86 \cdot \dot{\gamma}^{0.363}$
39.5	$\tau = 1.5 \cdot \dot{\gamma}^{0.435}$

From the analysis of rheological equations can be observed the non-Newtonian behavior with yield point τ_0, similar to the yield-pseudoplastic fluids, with flow exponent $n<1$. Also, for the samples with $\tau_0 \neq 0$, it is observed that the temperature increasing leads to the increase of the shear stress values, with preservation of non-Newtonian behavior.

A particular situation presents $PA_{2.5\text{-}8}$ sample to t= 39.5°C, to which is noticed the shape curve change with the shear rate increasing. For the presumptive inflection point corresponding to $\dot{\gamma}=215.7\,s^{-1}$ and $\tau=19.5\,Pa$ the apparent viscosity is obtained $\eta_a=\tau/\dot{\gamma}=0.09\,Pa\cdot s$ and, taking into account the geometrical dimensions of S/S_1 system, the calculated Ta_{Re} value is 0.75 (laminar domain being for $Ta_{\mathrm{Re}} \leq 60$) [3].

In Figures 2 and 3 is shown the $\tau=f(\dot{\gamma})$ dependence for PC_1 and PC_5 solutions at different temperature values, and in Table 5 are the obtained rheological equations.

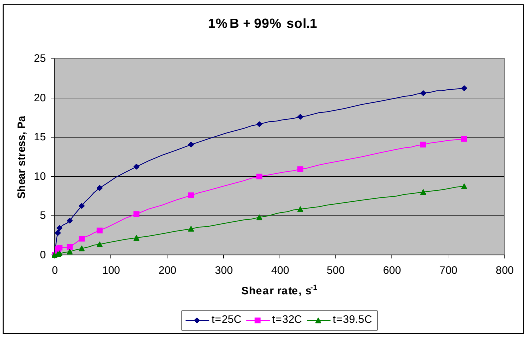

Figure 2. Dependence $\tau=f(\dot{\gamma})$ for sample PC_1

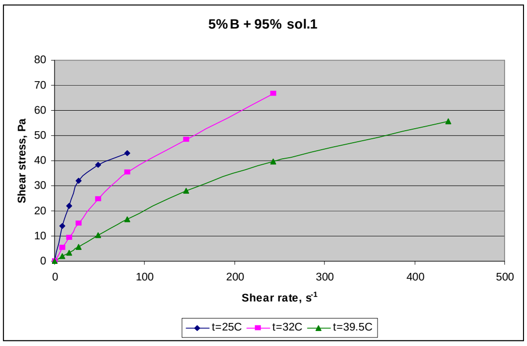

Figure 3. Dependence $\tau=f(\dot{\gamma})$ for sample PC_5

Table 5. Rheological equations for PC_{1-5} solutions

Temperature, ˚C	Equation		
	PC_1	PC_4	PC_5
25	$\tau = 1.4 \cdot \dot{\gamma}^{0.414}$	$\tau = 19.7 \cdot \dot{\gamma}^{0.185}$	$\tau = 6.6 \cdot \dot{\gamma}^{0.439}$
32	$\tau = 0.25 \cdot \dot{\gamma}^{0.618}$	$\tau = 3.9 \cdot \dot{\gamma}^{0.500}$	$\tau = 2.1 \cdot \dot{\gamma}^{0.630}$
39.5	$\tau = 0.04 \cdot \dot{\gamma}^{0.802}$	$\tau = 0.55 \cdot \dot{\gamma}^{0.810}$	$\tau = 0.74 \cdot \dot{\gamma}^{0.715}$

Through the measurements achievement at different temperatures it was possible to establish the dependence $\ln\tau = f(1/T)$ and to calculate the E_a values. For PC_{1-5} solutions, the E_a changes with the content of surfactant B is shown in Figure 4. It is observed that there is a range of concentrations at which E_a has minimum values minimum values of $(25 \div 65)\,kJ \cdot mol^{-1}$.

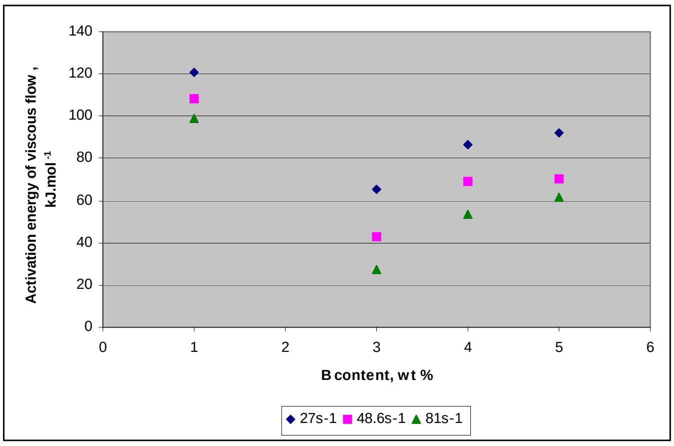

Figure 4. The activation energy evolution for PC_{1-5} samples

2. The preservation time influence

That influence was studied for sample PC_2 at 32°C, and $\tau = f(\dot{\gamma})$ dependence is presented in Figure 5. It can be observed that preservation does not change the non-Newtonian behavior but increases the shear stress values.

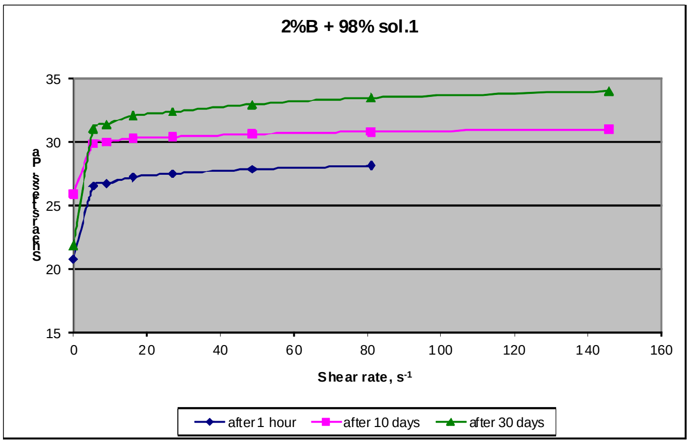

Figure 5. Dependence $\tau = f(\dot{\gamma})$ for sample PC_2 (t=32°C)

3. The influence of the amphiphilic surfactant VB

For samples $PA_{3\text{-}9}$, $PA_{3\text{-}10}$ and $PA_{3\text{-}12}$, in Figure 6, is shown the $\tau = f(\dot{\gamma})$ dependence, and the evolution of apparent viscosity with amphiphilic surfactant content is shown in Figure 7. From the obtained rheological equations (Table 6) is observed the non-Newtonian behavior specific to yield-pseudoplastic fluids, and the increase of apparent viscosity with increasing the concentration of amphiphilic component, respectively.

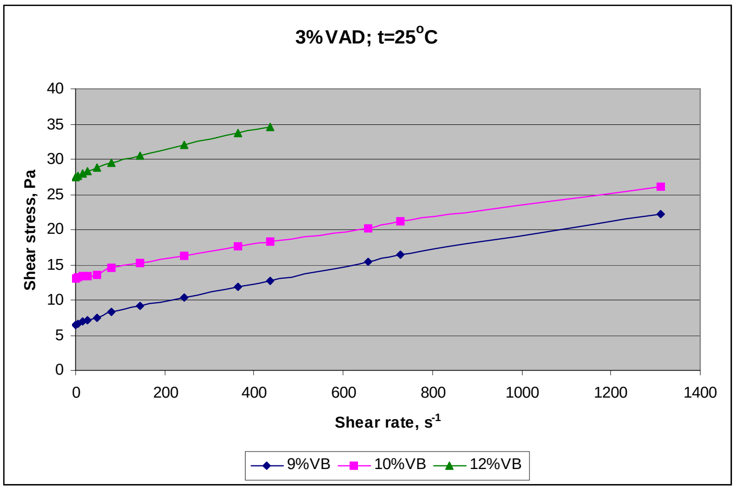

Figure 6. Dependence $\tau = f(\dot{\gamma})$ for $PA_{3\text{-}9}$, $PA_{3\text{-}10}$ and $PA_{3\text{-}12}$

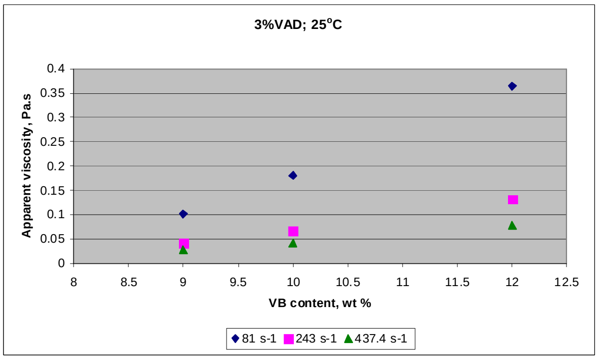

Figure 7. The apparent viscosity vs. the VB concentration

Table 6. Rheological equations for $PA_{3\text{-}9}$, $PA_{3\text{-}10}$ and $PA_{3\text{-}12}$ solutions (t =25˚C)

VB content, wt%	Equation
9	$\tau = 6.5 + 0.040 \cdot \dot{\gamma}^{0.824}$
10	$\tau = 13.1 + 0.034 \cdot \dot{\gamma}^{0.830}$
12	$\tau = 27.4 + 0.081 \cdot \dot{\gamma}^{0.740}$

The evolution of apparent viscosity of the solutions with 2%VAD and different percentages of the VB ($PA_{2\text{-}7}$ and $PA_{2\text{-}10}$) is shown in Figure 8.

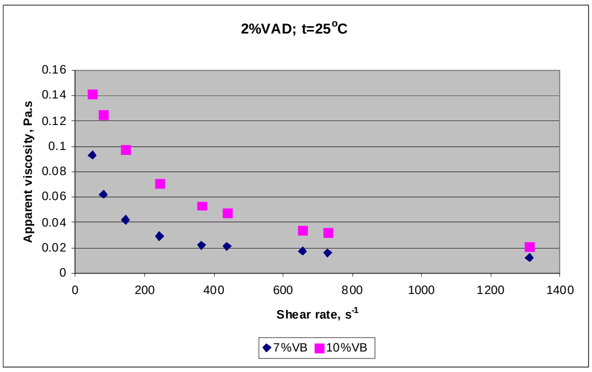

Figure 8. The apparent viscosity vs. shear rate

The obtained viscosity curves, with apparent viscosity decreasing with the increase of shear rate, show specific pseudoplastic behavior. It is also found in this case that increase of VB amphiphilic surfactant concentration increases the apparent viscosity. Also, at the same temperature, the solutions with 3%VAD have apparent viscosities higher than 2% VAD samples.

4. The influence of weakly cationic (VAD) or anionic (VA) surfactant

The evolution of apparent viscosity of samples with 10%VB and different percentages of VAD ($PA_{2\text{-}10}$, $PA_{2.5\text{-}10}$, $PA_{3\text{-}10}$) is shown in Figure 9.

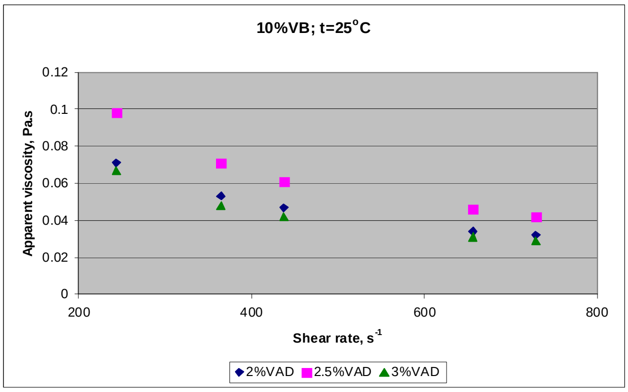

Figure 9. The apparent viscosity vs. shear rate

In Figure 10 is shown the shear stress dependence of shear rate for solutions containing 10%VB and 3%VA (P_{42}) [4] and 3%VAD ($PA_{3\text{-}10}$), respectively, at two temperatures. The obtained rheological equations are shown in Table 7. The non-Newtonian behavior is maintained, regardless of surfactant type (anionic or weakly cationic), but in the case of cationic one the shear stress increases with temperature increasing.

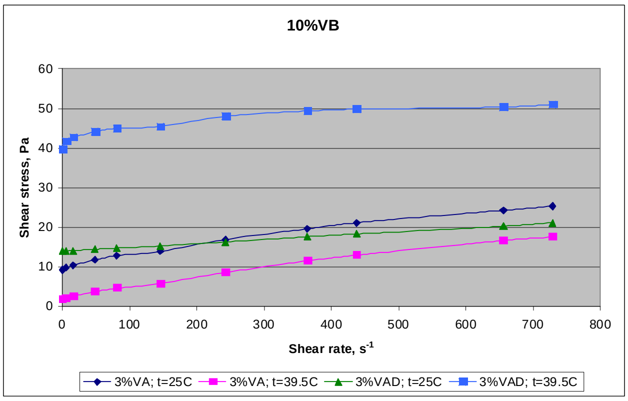

Figure 10. Dependence $\tau = f(\dot{\gamma})$ for samples P_{42} and $PA_{3\text{-}10}$

Table 7. Rheological equations for P_{42} and PA_{3-10}

Surfactant	Equation	
	25°C	**39.5°C**
3% VA	$\tau = 9.2 + 0.16 \cdot \dot{\gamma}^{0.707}$	$\tau = 1.7 + 0.09 \cdot \dot{\gamma}^{0.788}$
3% VAD	$\tau = 13.9 + 0.01 \cdot \dot{\gamma}$	$\tau = 39.7 + 1.1 \cdot \dot{\gamma}^{0.356}$

CONCLUSIONS

The rheological behavior of solutions based on active-surface agents was studied, monitoring the influence of the nature and concentration of surfactants, temperature and preservation time.

Specific rheological equations $\tau = \tau_0 + K \cdot \dot{\gamma}^n$ were established, showing non-Newtonian (pseudoplastic and yield-pseudoplastic) behavior of analyzed samples.

Increasing temperature and preservation time does not change the non-Newtonian nature of $\tau = f(\dot{\gamma})$ dependence.

EXPERIMENTAL SECTION

Determinations were made using the viscometer Rheotest-2 with the system vat-drum S/S_1, in temperature range 25÷40°C.

The samples were analyzed after one hour of preparation. Conservation of these solutions, at room temperature (~25°C), for 2-3 months has not led to significant changes in rheological properties.

REFERENCES

1. D-G Choi, W-J Kim, S-M Yang, *Korea-Australia Rheological Journal,* **2000,** *12,* 143.
2. N.Borş, "Contribuţii la studiul influenţei unor substanţe chimice asupra îmbunătăţirii curgerii lichidelor", Teză de doctorat, Univ."Politehnica" Timişoara, **2010.**
3. N.Borş, A. Tămaş, *Studia Univ. Babes-Bolyai Seria Chemia,* **2010**, *55(3)*, 139. A.Tămaş, M. Vincze, *Studia Univ. Babes-Bolyai Seria Chemia*, **2011** *(submitted).*