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

ANDRA TĂMAŞ[a], MARTIN VINCZE[b]

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.

Keywords: *real plastic behavior, shear rate, shear stress, surface-active agents*

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, which become hydrated in contact with water, undergoing a "swelling" process followed by the clogging of the well [1-3].

In order to increase the layer's 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), their main disadvantage being the difficult removal from the deposit's cracks after the solid material sedimentation [3-6].

Subsequently, viscoelastic solutions were used, characterized by a very good carrying capacity for the solid material, which, in contact with crude oil, suddenly lose their viscoelastic properties (due to the change of micelar structure), leave the solid in the cracks and are then eliminated from those [5,7]. The well-known viscoelastic fluids are the solutions with cationic surfactants content [7].

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[a] *Universitatea "Politehnica" din Timişoara, Facultatea de Chimie Industrială şi Ingineria Mediului, P-ța Victoriei 2, RO-300006 Timişoara, România, andra.tamas@chim.upt.ro*

[b] *vinczemartin@hotmail.com*

Viscoelasticity may be caused by the forming process of the micelles in this case, which is different from that related to the usual ones, which are spherical [8]. Viscoelastic fluids based on surface-active agents formed very long flexible ("wormlike") cylindrical micells in solutions, which confer them useful rheological properties.

The preparation of solutions was done by dispersing water (W) under intense stirring in surfactants mixture (VA+VB and VAD+VB, respectively) at room temperature (t~25°C). The main characteristics of the surface-active agents are found in Table 1, and the compositions of the solutions obtained are presented in Table 2. The critical micellar concentration (CMC) has been determined of VA and VB aqueous solutions with different concentrations.

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

Symbol	**Type**	**Active substance %**	**Molecular weight,** $kg \cdot kmol^{-1}$	**CMC,** $mol \cdot L^{-1}$	**pH of 1% aq. solution**
VA	anionic	35	362	$1.5 \cdot 10^{-3}$	7÷8
VB	amphiphilic	30	355	$8.7 \cdot 10^{-4}$	7÷7.5
VAD	weakly cationic	100	488	-	-

Table 2. The composition of solutions with VA content

Symbol	**Compozition, wt %**	**Symbol**	**Compozition, wt %**
P_{12}	3%VA+2%VB+95%W	P_{14}	5%VA+2%VB+93%W
P_{22}	3%VA+6%VB+91%W	P_{24}	5%VA+6%VB+89%W
P_{32}	3%VA+8%VB+89%W	-	-
P_{42}	3%VA+10%VB+87%W	P_{44}	5%VA+10%VB+85%W
P_{52}	3%VA+12%VB+85%W	P_{54}	5%VA+12%VB+83%W
P_{62}	3%VA+16%VB+81%W	P_{64}	5%VA+16%VB+79%W

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 viscous flow energy 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), shear rate, liquid density and apparent viscosity [9]:

$$Ta_{\mathrm{Re}} = \frac{\dot{\gamma} \cdot (r_o - r_i)^2 \cdot \rho}{\eta_a} \tag{1}$$

RESULTS AND DISCUSSION

The influence of temperature on the rheological behavior was determined for samples P_{22}, P_{42}, P_{52} and P_{62} (with 3%VA) and for samples P_{44}, P_{54} and P_{64} (with 5% VA). In Figures 1 and 2, dependence $\tau = f(\dot{\gamma})$ is shown, at three temperature values, for solution P_{52} and P_{54}.

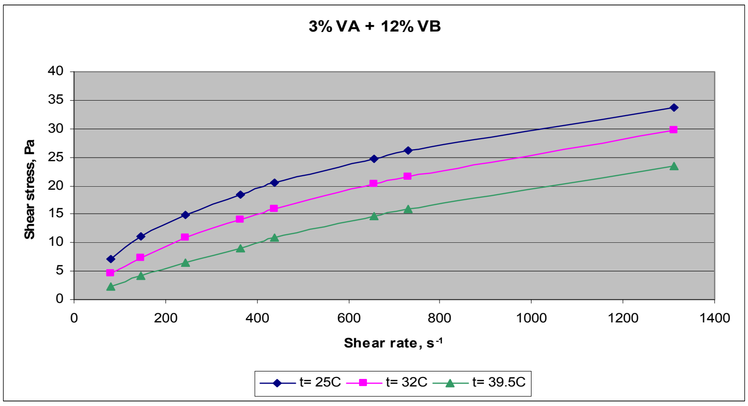

Figure 1. Dependence $\tau = f(\dot{\gamma})$ for P_{52} sample at different temperatures

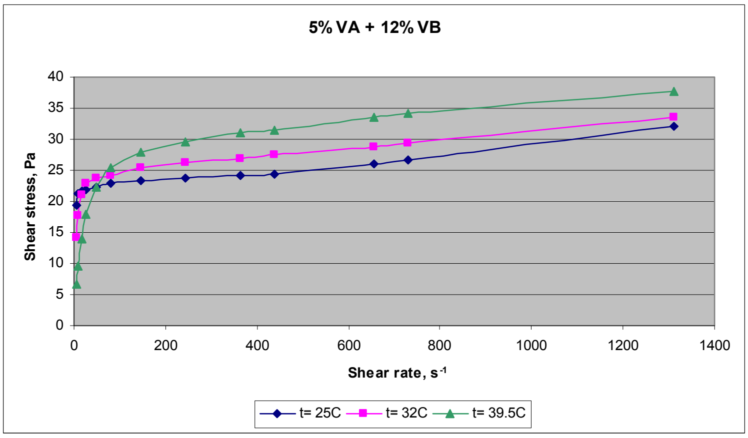

Figure 2. Dependence $\tau = f(\dot{\gamma})$ for P_{54} sample at different temperatures

The rheological equations are presented in Tables 3 and 4 for different $\dot{\gamma}$ range of values due to the change of curves inclination ($\dot{\gamma}_{ch}$ is the value of transition).

From the analysis of rheological equations for all solutions, the non-Newtonian behavior can be observed, similar to the real plastic fluids ($n<1$). Also, it was observed the decrease of coefficient K and the increase of the exponent n with the temperature increase (for P_{54} only for $\dot{\gamma}<48.6s^{-1}$), while the non-Newtonian behavior is maintained. The Ta_{Re} values increase with the temperature increase. For sample P_{54} is found that the shear stress increases as the temperature increases, as well as the change of curves slope at lower values of the shear rate.

Table 3. Rheological equations for P_{52} sample at various temperatures

Temp., °C	**Equation** $\tau = K \cdot \dot{\gamma}^n$	**r²**	$\dot{\gamma}_{ch}$, **s⁻¹**	**Ta$_{Re}$**
25	$\tau = 0.4 \cdot \dot{\gamma}^{0.660}$, $\dot{\gamma} \in (81 \div 243)s^{-1}$	0.9944	283.4	0.77
	$\tau = 1.2 \cdot \dot{\gamma}^{0.466}$, $\dot{\gamma} \in (364.5 \div 1312)s^{-1}$	0.9979		
32	$\tau = 0.14 \cdot \dot{\gamma}^{0.793}$, $\dot{\gamma} \in (81 \div 243)s^{-1}$	0.9998	281.9	1.04
	$\tau = 0.46 \cdot \dot{\gamma}^{0.583}$, $\dot{\gamma} \in (364.5 \div 1312)s^{-1}$	0.9986		
39.5	$\tau = 0.033 \cdot \dot{\gamma}^{0.976}$, $\dot{\gamma} \in (81 \div 243)s^{-1}$	0.9983	292.1	1.72
	$\tau = 0.12 \cdot \dot{\gamma}^{0.735}$, $\dot{\gamma} \in (364.5 \div 1312)s^{-1}$	0.9964		

Table 4. Rheological equations for P_{54} sample at various temperatures

Temp., °C	**Equation** $\tau = K \cdot \dot{\gamma}^n$	**r²**	$\dot{\gamma}_{ch}$, **s⁻¹**	**Ta$_{Re}$**
25	$\tau = 19.7 \cdot \dot{\gamma}^{0.032}$, $\dot{\gamma} \in (9 \div 48.6)s^{-1}$	0.9985	10.1	0.00077
	$\tau = 11.3 \cdot \dot{\gamma}^{0.116}$, $\dot{\gamma} \in (81 \div 1312)s^{-1}$	0.9632		
32	$\tau = 10.7 \cdot \dot{\gamma}^{0.234}$, $\dot{\gamma} \in (9 \div 48.6)s^{-1}$	0.9798	23.9	0.0041
	$\tau = 6.8 \cdot \dot{\gamma}^{0.218}$, $\dot{\gamma} \in (81 \div 1312)s^{-1}$	0.9936		
39.5	$\tau = 3.4 \cdot \dot{\gamma}^{0.496}$, $\dot{\gamma} \in (9 \div 48.6)s^{-1}$	0.9830	70.6	0.032
	$\tau = 14.2 \cdot \dot{\gamma}^{0.133}$, $\dot{\gamma} \in (81 \div 1312)s^{-1}$	0.9849		

The dependence $\tau = f(\dot{\gamma})$ for the samples with 3% VA and various percentages of VB, at 39.5˚C, is expressed in Figure 3 and the rheological equations are presented in Table 5.

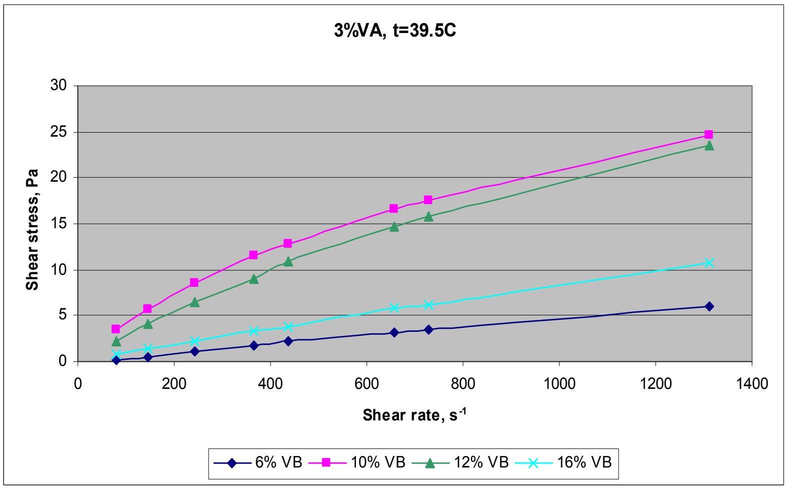

Figure 3. $\tau = f(\dot{\gamma})$ dependence for P_{22}, P_{42}, P_{52} and P_{62} samples

From Figure 3, for P_{22} and P_{62} samples it is observed that the $\tau = f(\dot{\gamma})$ dependence can be considered linear.

Table 5. Rheological equations for samples with 3% VA at 39.5˚C

Symbol	**VB content, wt %**	**Equation**	r^2
P_{22}	6	$\tau = 0.00475 \cdot \dot{\gamma}$	0.9952
P_{42}	10	$\tau = 0.17 \cdot \dot{\gamma}^{0.70}$	0.9925
P_{52}	12	$\tau = 0.06 \cdot \dot{\gamma}^{0.84}$	0.9942
P_{62}	16	$\tau = 0.0081 \cdot \dot{\gamma}$	0.9988

From the graphical representation of $\tau / \dot{\gamma}$ evolution as a function of shear rate for solutions with 3%VA (Figure 4) it is observed that the ratio decreases with the increase of $\dot{\gamma}$ (for samples with 10% and 12%VB). The apparent viscosity of the sample with 6%VB is significantly smaller than the other samples and decreases with the shear rate increase only at $\dot{\gamma} > 437.4 s^{-1}$. For samples containing 5%VA, in the same conditions, the apparent viscosity is significantly higher than 3%VA samples and decreases with the shear rate increase (Figure 5).

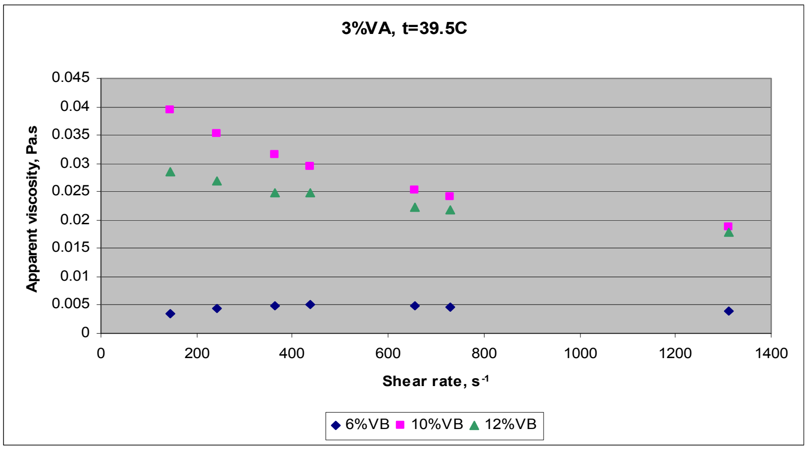

Figure 4. $\tau/\dot{\gamma} = f(\dot{\gamma})$ dependence for P_{22}, P_{42}, and P_{52} samples

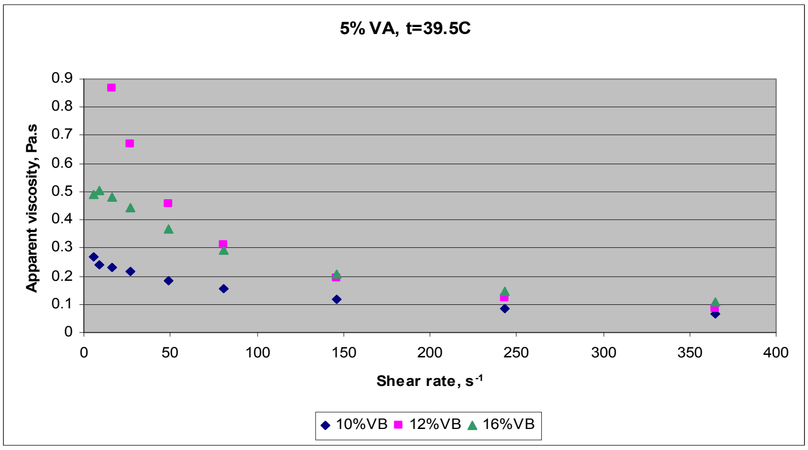

Figure 5. $\tau/\dot{\gamma} = f(\dot{\gamma})$ dependence for P_{44}, P_{54}, and P_{64} samples

The temperature increase leads to microdrops mobility intensification which influences the activation energy of the system. The phenomenon can be explained by Arhenius type equation applied to the cumulative effect described by the shear stress (eq. 2):

$$\tau = A' \cdot e^{\frac{E_a}{R \cdot T}} \tag{2}$$

where: A' - preexponential coefficient having the dimension of shear stress; E_a - activation energy; R - general gas constant; T - absolute temperature.

The study of the influence of temperature on the activation energy of the system was done for all the analyzed solutions. Dependence $\ln\tau = f(1/T)$ was graphically represented, as obtained from the logarithmic form of equation (2), for shear stress values corresponding to the three chosen values of the shear rate.

Particular expressions of equation (2) for solutions with 3%VA are presented in Table 6.

Table 6. Particular expression of eq. (2) for samples P_{22}, P_{52} and P_{62}

$\dot{\gamma}\ s^{-1}$	**Equation** $\tau = A^{'} \cdot \exp(E_a/R \cdot T)$		
	P_{22}	**P_{52}**	**P_{62}**
145.8	$\tau = 5.6 \cdot 10^{-17} \cdot \exp(11.5/T)$	$\tau = 7.6 \cdot 10^{-9} \cdot \exp(3.0/T)$	$\tau = 1.9 \cdot 10^{-5} \cdot \exp(3.5/T)$
243	$\tau = 9.8 \cdot 10^{-14} \cdot \exp(9.4/T)$	$\tau = 3.6 \cdot 10^{-7} \cdot \exp(5.2/T)$	$\tau = 6.8 \cdot 10^{-6} \cdot \exp(3.9/T)$
729	$\tau = 2.4 \cdot 10^{-10} \cdot \exp(7.3/T)$	$\tau = 5.3 \cdot 10^{-4} \cdot \exp(3.2/T)$	$\tau = 6.0 \cdot 10^{-5} \cdot \exp(3.6/T)$

In Figure 6 the activation energy change is shown as related to the VB content for solutions with 3% VA.

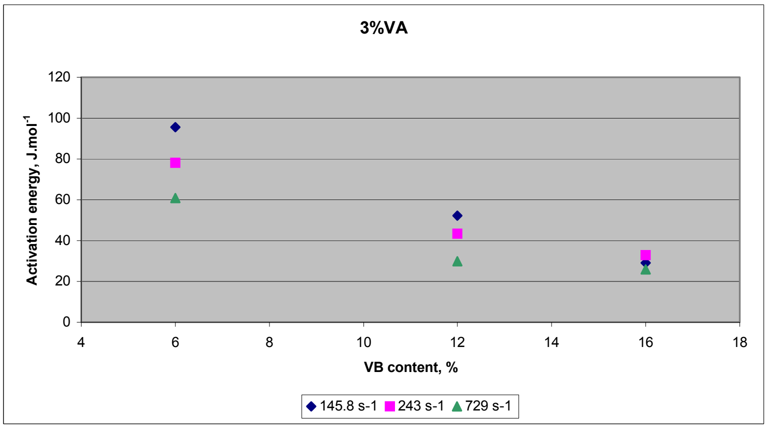

Figure 6. Activation energy changes for P_{22}, P_{52} and P_{62} samples

The variation of Ta_{Re} number with temperature and the VB content, respectively, is shown in Figure 7.

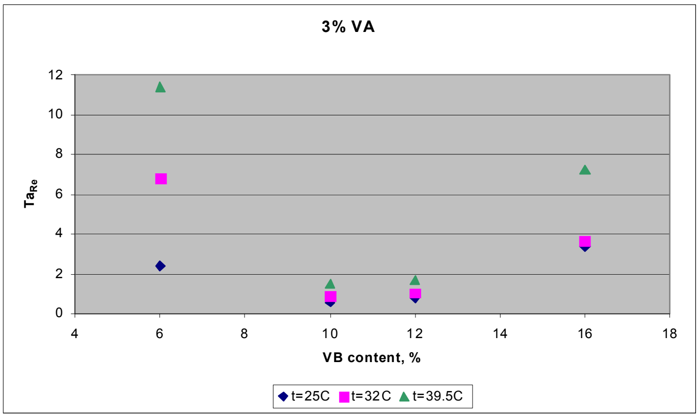

Figure 7. Ta_{Re} evolution for samples with 3% VA

CONCLUSIONS

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

The rheological characterization was carried out in thermostatic conditions, using a rotational viscometer Rheotest-2 which correlates the shear stress value τ with the shear rate $\dot{\gamma}$. Specific rheological equations $\tau = K \cdot \dot{\gamma}^n$ were established.

P_{12}, P_{14} and P_{24} solutions could not be analysed using Rheotest-2 viscometer, as being too little viscous.

The temperature increase does not change the non-Newtonian nature of $\tau = f(\dot{\gamma})$ dependence, but leads to the increase of the shear stress value for samples with 5%VA. For the samples with 3%VA, the temperature increase leads to the decrease of exponent n and the increase of K.

The activation energy values decrease as the content of VB component and shear rate increase, which corresponds with the increase of Ta_{Re} number (according to the intensification of system turbulence).

For all temperatures there is a range of concentrations at which Ta_{Re} number has minimum values.

EXPERIMENTAL SECTION

Using the stalagmometer method (drop weight method) the surface tension has been determined of VA and VB aqueous solutions with different concentrations. From the dependence between the surface tension σ and the concentration c natural logarithm the corresponding values of CMC were established.

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 immediately after preparation. Conservation of these solutions, at room temperature, for 2-3 months has not led to significant changes in rheological properties.

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