Aqueous Solutions of Polyethoxylated Fatty Alcohols
Rheological behavior and superficial properties

ANDRA TAMAS, SABINA NITU*
Politehnica University Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 V. Parvan Blvd., 300223, Timisoara, Romania

The paper presents the study of the rheological and superficial behavior (foaming power and wetting capacity) of some aqueous solutions with polyethoxylated fatty alcohols content. The influence of fatty alcohols concentration and their degree of ethoxylation as well as that of temperature on the rheological behavior was determined from the dependences between the shear stress $\tau$ and the shear rate $\dot{\gamma}$. The results demonstrate that all the studied solutions have non-Newtonian behavior, with flow behavior index smaller than 1.

Keywords: apparent viscosity, non-Newtonian behavior, polyethoxylated alcohols

Polyethoxylated fatty alcohols are probably the most important group of nonionic surfactants due their rapid biodegradability and low toxicity of metabolites. They have hydroxyl or ether bond which will not ionize in water [1]. Polyethoxylated alcohols are based on synthetic or natural fatty alcohols and have the general formula R-CH$_2$O-(CH$_2$-CH$_2$-O)$_n$-H, where R represents the alkyl group of the parent alcohol and n is the number of the ethoxyl units. Natural polyethoxylated fatty alcohols generally contain C$_6$-C$_{18}$ linear chains. The degree of ethoxylation as well as the chain length, branching and saturation decide on the surface activity and other physical properties of ethoxylated alcohols [2,3].

C$_{16}$/C$_{18}$ fatty alcohol (cetostearyl) ethoxylates is used as detergents in heavy-duty washing powders, as dispersing agents and solubilizers, as wetting agents for industrial applications in aqueous solutions, as emulsifiers for O/W - emulsions of oils, fats, paraffin, polyolefin waxes and silicone oil emulsions and as emulsifiers for emulsion polymerization [4-6]. Ethoxylated products influence the stability of emulsions by altering the solubility and flow characteristics [7].

The aim of this work was to analyze the rheological behavior of aqueous solutions with various concentrations of polyethoxylated fatty alcohols. It was followed the influence of surfactant concentration and degree of ethoxylation, as well as that of temperature, on the rheological behavior. In addition, rheological relations $\tau= f(\dot{\gamma})$ were established, and it was calculated the activation energy of viscous flow.

Experimental part
For the preparation of aqueous solutions of nonionic surfactants, fatty alcohol C$_{16}$/C$_{18}$ ethoxylated with 50 (AGE$_{50}$) and 20 (AGE$_{20}$) moles of ethylene oxide respectively, was used. The main physicochemical properties of these products are given in table 1.

The samples preparation was done at 50°C, by dispersing the nonionic surfactant in water with a mechanical stirrer with diameter 45mm, which provides an intense stirring ($Re=5\times10^4$) corresponding to a peripheral velocity of 3.5 m s$^{-1}$. The composition of the samples is presented in table 2.

The rheological measurements were carried out under thermostatic conditions, at different temperatures ranging from 25 to 50°C, using a Rheotest-2 rotation viscometer with the system vat-drum S/S, suitable for the viscosity range of these fluids and higher sensibility. The device allows the measurement of the torsion moment appeared thanks to the ring-shaped substance layer placed between a fixed cylinder and a rotating one with known revolution. The torsion moment is correlated with the shear stress. The revolution and the ring-shaped layer thickness determine the shear rate. Shear rate values were changed in the range $81 \div 1312$ s$^{-1}$. The samples were analysed after one day of preparation.

Table 1
THE PROPERTIES OF ETHOXYLATED FATTY ALCOHOLS [8,9]

| Property                  | Conditions of admisibility/Value |
|--------------------------|----------------------------------|
| Average molecular weight, g mol$^{-1}$ | 243107                        |
| Appearance at 25°C       | White waxy solid (flakes)       |
| Physical state changement, °C | 52.56                         |
| Cloud point (1% in 10% NaCl), °C | 74.78                         |
| pH of aq. sol. 3%        | 5-7                             |
| Ethylene Oxide content, % w/w  | 89.57                         |
| HLB                      | 17.8                           |
| Hydroxyl number, mg KOH g$^{-1}$ | 21.27                         |
| Kinematic viscosity, cSt | 102 (70°C)                     |

* email: sabina.nitu@upt.ro; Phone: 0256404231

382 [http://www.revistadechimie.ro](http://www.revistadechimie.ro) REV.CHIM.(Bucharest) ● 70 ● No. 2 ● 2019
Results and discussions

The influence of temperature on the rheological behavior was determined for all the samples. In figure 1, dependence $\tau=f(\dot{\gamma})$ is shown, at three temperature values, for solution A3 (12.5 wt.% AGE_{50}) and B3 (12.5 wt.% AGE_{20}).

The obtained rheological equations are shown in table 3 and suggest that these solutions have a pseudoplastic behavior, which corresponds to the Ostwald de Waele rheological model [10-13]:

$$\tau = K \cdot \dot{\gamma}^n$$

(1)

where $K$ is the consistence coefficient and $n$ is the flow index.

Both the graphical representation and the values of the flow index show that, at the same temperature, the samples containing AGE_{50} exhibit higher shear stress values than those with AGE_{20}.

From the graphical representation of apparent viscosity $\eta_a$ (calculated as the ratio between the shear stress and the shear rate) evolution as a function of shear rate for samples A3 and B3 (fig. 2) it is observed that the ratio decreases slightly with the increase of shear rate. However, the apparent viscosity decreases more pronounced with increasing temperature.

The increase in temperature of fluid will enhances the mobility of the molecules and increase in inter-molecular spacing, which decreases its flow resistance [14]. The phenomenon can be explained by an Arrhenius type equation applied to the cumulative effect described by the shear stress:

$$\tau = A' \cdot e^{E_a/R \cdot T}$$

(2)

where $E_a$ is the activation energy of viscous flow (J mol$^{-1}$); $R$ -the gas constant (J mol$^{-1}$ K$^{-1}$); $T$ -absolute temperature (K); $A'$ represents the material constant (Pa s).

| Sample | Temperature, °C | $E_a$ (J mol$^{-1}$) | $K$ | $A'$ (Pa s) |
|--------|-----------------|----------------------|-----|-------------|
| A3     | 25              | 0.0224 - 0.9944      | 0.59995 |             |
|        | 30              | 0.0154 - 0.9972      | 0.99987 |             |
|        | 35              | 0.01 - 0.9965        | 0.99965 |             |
| B3     | 25              | 0.011 - 0.9933       | 0.99971 |             |
|        | 30              | 0.0116 - 0.9855      | 0.99716 |             |
|        | 35              | 0.0105 - 0.9835      | 0.99716 |             |

The correlation coefficient

$\log \dot{\gamma}$

$\log \eta_a$

![Fig. 1. Shear stress vs. shear rate for samples A3 and B3](image1)

![Fig. 2. Apparent viscosity vs. shear rate for samples A3 and B3](image2)
Table 4
PARAMETERS OF ARRHENIUS EQUATION

| $\dot{\gamma}$, s⁻¹ | Eq. $\tau = A \cdot \exp(E_a / \mathcal{R} \cdot T)$ | $A_3$ | $A_4$ | $A_5$ | $B_3$ | $B_4$ | $B_5$ |
|---------------------|------------------------------------------------|-------|-------|-------|-------|-------|-------|
| 145.8               | $\tau = 5.5 \cdot 10^{-3} \cdot \exp(5256 / T)$|       |       | 30.5  | 30.5  | 30.5  | 30.5  |
| 437.4               | $\tau = 9.9 \cdot 10^{-5} \cdot \exp(4012 / T)$|       |       | 728    | 728    | 728    | 728    |
| 1312                | $\tau = 2.2 \cdot 10^{-6} \cdot \exp(3400 / T)$|       |       | 1847   | 1847   | 1847   | 1847   |

Table 5
RHEOLOGICAL EQUATIONS FOR SAMPLES B1-5 AT 25°C

| Sample | Eq. $\tau = K \cdot \dot{\gamma}^n$ | $\mathcal{R}^2$ |
|--------|----------------------------------|----------------|
| B1     | $\tau = 0.038 \cdot \dot{\gamma}^{0.023}$ | 0.99304 |
| B2     | $\tau = 0.0276 \cdot \dot{\gamma}^{0.717}$ | 0.99911 |
| B3     | $\tau = 0.02 \cdot \dot{\gamma}^{0.013}$ | 0.99979 |
| B4     | $\tau = 0.0279 \cdot \dot{\gamma}^{0.628}$ | 0.99995 |
| B5     | $\tau = 0.058 \cdot \dot{\gamma}^{0.685}$ | 0.99997 |

The parameters of Arrhenius model equation which were determined from the logarithmic form of equation (2) ($\ln \tau = f(1 / T)$), for shear stress values corresponding to the three chosen values of the shear rate, are reported in table 4.

It can be seen that for all the solutions the increase of shear rate leads to the increase of the pre-exponential coefficient $A$ and the decrease of the activation energy. A possible explanation of the decrease in activation energy with the increase of the shear rate would be that higher velocity leads to higher turbulence and dynamic pressure, with effect on the decrease of the molecular associations and their relaxation period. At the same ethoxylated alcohol concentration, the samples with AGE_20 content (B3-B5) exhibit higher values for the activation energy of viscous flow.

The influence of surfactant concentration on rheological behavior was studied for the samples containing AGE_20 at 25°C. The obtained rheological equations are shown in table 5.

It can be noticed that regardless of the concentration, the rheological behavior is pseudoplastic, more pronounced at lower concentrations ($n < 0.8$).

The variation of apparent viscosity of these solutions is shown in figure 3. It is noted that the apparent viscosity decreases with the increase of shear rate, more pronounced at the more dilute solutions (15.7% at B1) and less at the most concentrated (2.1% at B5, at 25°C). Also, the apparent viscosity increases with the increase of the surfactant concentration. The consistency of the solutions increases substantially at concentrations above 15%, reaching the consistency of a gel at concentrations greater than 20%.

In figure 4 is shown the influence of the degree of ethoxylation of fatty alcohols on the apparent viscosity of their solutions.

Polyethoxylated nonionic surfactants generally produce less foam and much less stable foam than ionic surfactants in aqueous media. These effects are probably due to the larger surface area per molecule and the absence of highly charged surface films in these foams [15].

The foaming power and wetting capacity of the two ethoxylated fatty alcohols were studied for aqueous solutions having concentrations ranging from 0.25 wt.% to 4 wt.%, higher than critical micelle concentration (CMC) [16,17].
Figures 5a and 5b show the volume of foam after 30 s and 5 min respectively, depending on the surfactant concentration.

The variation of wetting capacity, expressed as average wetting time, depending on the concentration of the solution is shown in figure 6.

This variation highlights lower wetting times for AGE_20 more efficient than AGE_50, the wetting capacity increases with the concentration of the solution up to 1 wt.%, after which it remains constant on the studied concentration range, although for AGE_50 the same limitation of wetting capacity is observed starting with the concentration of 3 wt.%.

Conclusions
The analysed samples present non-Newtonian behavior.
with flow behavior index smaller than 1, regardless of temperature, concentration of fatty alcohol and degree of ethoxylation. The decrease of apparent viscosity with increasing of shear rate is more pronounced at lower temperatures and in more dilute solutions.

For both polyethoxylated alcohols the volume of foam increases slightly with increasing concentration to ~ 1 wt.%, after which it remains approximately constant across the studied range of concentration, figure 5a.

At low concentrations, less than 0.5 wt.%, the differences in the volume of foam are insignificant, but with increasing concentrations they increase in favor of AGE_50. These differences are even greater after 5 minutes (fig. 5b), which shows that the foam stability is higher for the surfactant with higher degree of polyethoxylation.

The results could be explained by the adoption of a helicoidal form of polyethoxylated chains in the aqueous phase which provides a greater number of cohesion forces for AGE_50 and hence a greater mechanical strength and elasticity of the film. This variation is also explained by the lower values of surface tension for the solutions with concentration 0.25 wt.% ($\gamma_{AGE_{50}} = 51.25 \text{ mN m}^{-1}$, $\gamma_{AGE_{20}} = 53.53 \text{ mN m}^{-1}$).

References
1. FARN, R. J., Chemistry and Technology of Surfactants, Blackwell Publishing, Oxford, UK, 2006, p.136
2. ROSEN, M. J., KUNJAPPU, J. T., Surfactants and Interfacial Phenomena, 4th ed., John Wiley & Sons Inc., New Jersey, 2012, p. 24, 132
3.*** www.clariant.de/11.11.2013_Surfactants_Brochure_2013_final.pdf
4.*** www.clariant.de/2009_Construction_Newsroom_Brochures_Surfactants.pdf
5. POP, M. D., RO 116645 B, 2001
6. HOLMBERG, K., JONSSON B., LINDMAN, B., Surfactants and Polymers in aqueous solution, 2nd ed., John Wiley & Sons Ltd., Chichester, UK, 2003, p.97
7. OBUKOWHO, P., Ingredients and Their Role in Relaxer Formulations in: Hair Relaxers, Science, Design, and Application, 1st ed., Allured Pub Corp, 2012, p.77
8.*** http://www.tellerini.it/en/emuldac-alcs-100-sc-p361
9.*** http://interchimie.fr/data/catalog
10. RAO, M.A., Flow and Functional Models for Rheological Properties of Fluid Foods in: Rheology of Fluid, Semisolid, and Solid Foods-Principles and Applications, 3rd ed., Springer Science & Business Media NY, 2014, p.28
11. TUDOSE, R. Z., Ingineria proceselor fizice din industria chimica, vol. I, Ed. Academiei Române, Bucuresti, 2000, p. 124
12. TAMAS, A., PADURE, M., VINCZE, M., Rev. Chim. (Bucharest), 67, no. 2, 2016, p.344
13. MALINK, A.Ya., ISAYEV, A.I., Rheology: Concepts, Methods, and Applications, 2nd ed., Chem Tec Publishing Toronto, 2012, p.131
14. KUMAR, R., MANJUNATHA, S., KATHIRAVAN, T., VIJAYALAKSHMI, S., NADANASABAPATHI, S., RAJU, P.S., J. Food Sci. Technol., 52, nr.9, 2015, p.5611
15. ROSEN, M. J., Surfactants and Interfacial Phenomena, 2nd ed., John Wiley & Sons Inc., New Jersey, 1989, p. 288, 293
16.*** SR ISO 696: 1997
17.*** SR EN 1772:2009.

Manuscript received: 12.04.2018