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Antiseizure Properties of Aqueous Solutions of Ethoxylated Sorbitan Esters

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Influence of compound's type and concentration of ethoxylated sorbitan ester (ESE) water solutions on their anti-seizure properties was investigated. Ethoxylated sorbitan monolaurate (ESL), ethoxylated sorbitan monostearate (ESS) and ethoxylated sorbitan monooleate (ESO) were used as lubricant additives.

Tribological tests were performed on the four-ball machine, at linearly increasing load (409 N/s) (tribosystem: steel-steel). On the basis of the critical load (the load at the moment of rapid increment of friction torque) anti-seizure properties of the solutions were assessed. The other measured parameter was the seizure load that is load at the moment when friction torque exceeded 10 Nm.

According to the obtained results one can say that addition of ESE to water significantly improves its anti-seizure properties. The measured tribological quantities strongly depend on concentration. 1 %, 4 %, 10 %, 30 %, 50 %, and 100 % solutions were tested. The best anti-seizure properties were observed for 1 %, 4 %, 10 % solutions. The obtained results can be interpreted as a consequence of a formed liquid crystalline structure near to surface. Presence of meso-phases in the tested solutions was confirmed by observations in polarized light and characteristic changes of the viscosity.

Keywords: scuffing, seizure, ethoxylated sorbitan esters, lyotropic liquid crystals, lubricant additives.

1. INTRODUCTION

Liquid crystals are liquids in which a long-distance order exists. This is a thermodynamic state which differs from liquids, among other things, in optical, electric, magnetic and mechanical properties. The mesomorphic state in liquids was discovered, by F. Reinitzer in the second half of 20th century, and investigated by O. Lehman and R. Schenk. In 20th century liquid crystals found many applications in technology, physics, biology and medicine. Liquid crystals can arise by melting (thermotropic liquid crystals) and by solvatation (lyotropic liquid crystals).

Especially appealing is application of lyotropic liquid crystals in tribology. Compounds, which form mesomorphic structures, can be applied as lubricant additives [1 – 9]. Use of mechanical quantities anisotropy of these compounds would be very interesting. It can be predicted that heterogeneous, ordered structures are formed in both bulk and surface phases. In the first case these structures change rheology of lubricant, in the second case they influence changing friction conditions, decrease friction coefficient and wear of interacting elements.

The problem of applying compounds which can form liquid crystalline structures was investigated before [10 – 13]. Solutions of alkyl polyglucosides, sorbitan esters and ethoxylated sodium lauryl sulfate were analyzed. It was concluded that in most cases the concentration of the additive and its chemical structure decide about the ability to reduce friction coefficient, wear and to prevent seizure.

Influence of type of compounds and concentration of water solutions of ethoxylated sorbitan esters on antiseizure properties was tested.

2. EXPERIMENTAL

2.1. Lubricating medium

1 %, 4 %, 10 %, 30 % and 50 % aqueous solutions of ethoxylated sorbitan monolaurate (ESML), ethoxylated sorbitan monostearate (ESMS) and ethoxylated sorbitan monooleate (ESMO) were used as lubricants. Moreover, the tests were performed for pure water and pure esters. General formula of ethoxylated sorbitan monoesters is presented in Fig. 1.

For the tests we used sorbitan esters supplied by Cognis. Deionized water was applied as a lubricant base.

Ethoxylated sorbitan esters can form micelles at higher concentration, which is called the critical micelle concentration (CMC). A type of micelles formed depends on shape of a molecule. In our case, the length of an alkyl chain and the existence of unsaturated bonds have an influence on the shape of molecules. When a concentration is sufficiently high, the aggregates are regularly ordered. This phenomenon leads to a liquid crystalline state. Various phases are characterized by different viscosities. The correlation between viscosity and concentration of ESME water solutions is presented in Fig. 2 (Brookfield RV DVI+, 100 rpm, 20 °C).

For ethoxylated sorbitan monostearate (ESMS) and ethoxylated sorbitan monooleate (ESMO) solutions (at concentrations higher than 30 %) the increment in viscosity was observed. It is connected to forming liquid crystal phases. The existence of these mesophases was confirmed by polarization micrographs, (Polarization microscope, made by PZO Poland) (see Fig. 3).

For 50 % water solutions of ethoxylated sorbitan monolaurate (ESML) a liquid crystalline state was not observed.

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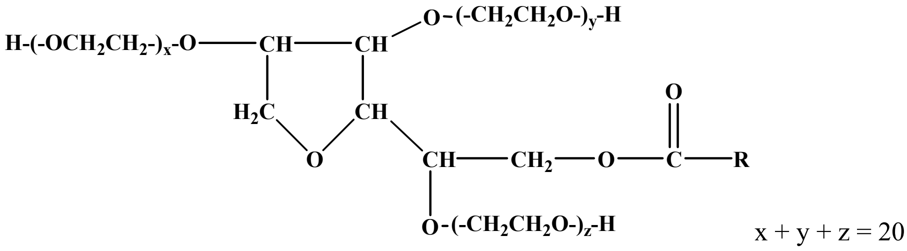


Fig. 1. Ethoxylated sorbitan ester (R – alkyl chain)

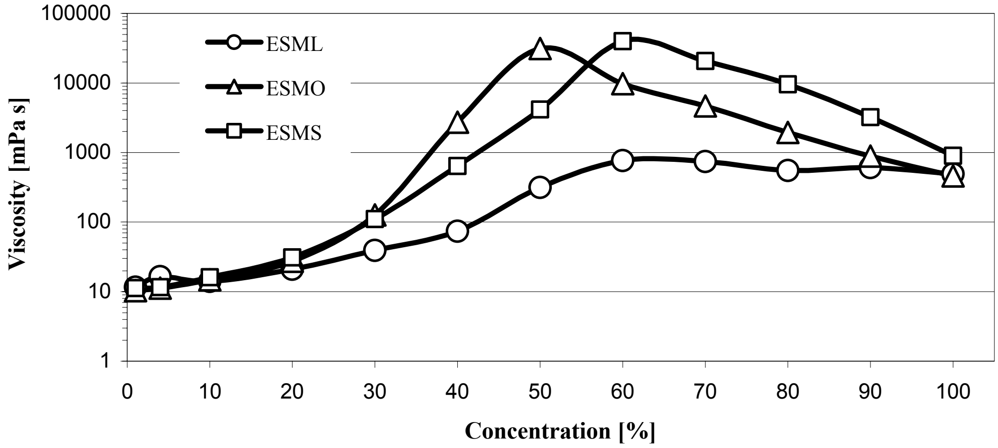
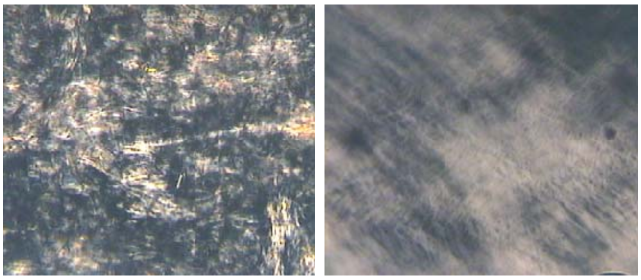


Fig. 2. Viscosity of aqueous solutions of ethoxylated sorbitan esters versus concentration (Brookfield RV DVI+, 100 rpm, 20 °C)



a b

Fig. 3. Polarization micrographs of ethoxylated sorbitan esters aqueous solutions: a – 50 % ESMS / water, b – 50 % ESMO / water (magnification 150×, temperature 20 °C)

2.2. Tribological tests

The tests were performed using the modified four-ball machine (made by Institute For Terotechnology in Radom, in accordance with Polish Norm PN-76/C-04147). The balls were made of ŁH15 steel with a diameter of ½”. Surface roughness was $R_a = 0.032$ µm and hardness 60 – 65 HRC. Before the test all the balls were chemically cleaned.

The tribological properties were investigated in the following conditions: rotating speed: 500 rpm, speed of load growth: 409 Ns^{-1}, initial load applied: 0 N, maximal possible load: 7200 N. On the basis of scuffing load (P_t), seizure load (P_{oz}) and limiting pressure of seizure (p_{oz}) antiseizure properties of aqueous solutions of ethoxylated sorbitan esters were assessed [14].

Scuffing load (P_t) - the load at the moment of rapid increment of friction torque. Seizure load (P_{oz}) – the load at the moment when friction torque exceeded 10 Nm.

Limiting pressure of seizure (p_{oz}) – parameter which was evaluated according to the formula:

$$p_{oz} = 0.52 \times P_{oz} / d^2 , \quad (1)$$

where P_{oz} is the seizure load, d is the wear scar diameter.

2.3. Analysis of the results

On the basis of the obtained results the dependence of scuffing load (P_t), seizure load (P_{oz}) and limiting pressure of seizure (p_{oz}) on concentration of water solutions of (ESML), (ESMS) and (ESMO) was evaluated.

Each value of the graphs is an averaged value of three independent tests. To evaluate bounds of the confidence interval for the mean friction coefficient in the specified intervals t-Student distribution was used. For each value of the graph a standard deviation was evaluated. Then, the bounds of the confidence intervals for all the values were derived for significance level equal to 0.9.

3. RESULTS

3.1. Antiseizure properties of ethoxylated sorbitan monolaurate water solutions

At the first stage of the work water solutions of (ESML) were analyzed.

On the basis of the performed tests dependence presented in Fig. 4 was obtained.

Addition of ESML to water improves its antiseizure properties. Up to 10 %, with increasing concentration of ESML, both scuffing load and seizure load increase. Further increasing of ester concentration does not improve anti-seizure properties.

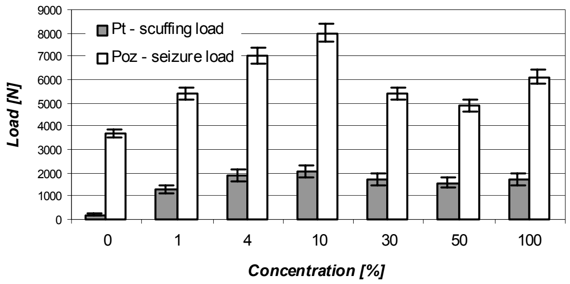


Fig. 4. Scuffing load P_t and seizure load P_{oz} versus concentration of water solutions of ethoxylated sorbitan monolaurate

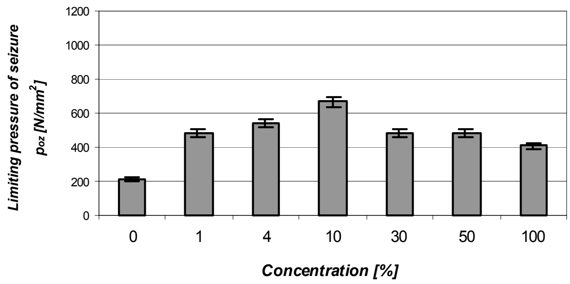


Fig. 5. Limiting pressure of seizure p_{oz} versus concentration of water solutions of ethoxylated sorbitan monolaurate

For limiting pressure of seizure (Fig. 5) the best properties were observed for 4 % and 10 % solutions.

3.2. Antiseizure properties of ethoxylated sorbitan monostearate water solutions

In the next stage of our experiment the influence of water solutions of ESMS on antiseizure properties was analysed. The results obtained are presented in Fig. 6.

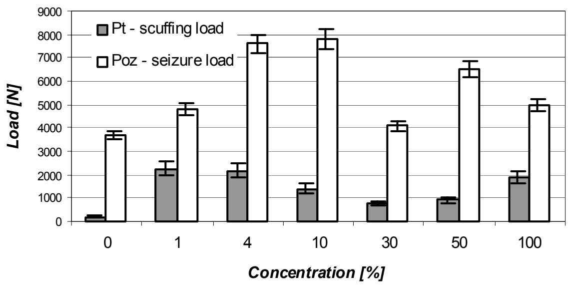


Fig. 6. Scuffing load P_t and seizure load P_{oz} versus concentration of water solutions of ethoxylated sorbitan monostearate

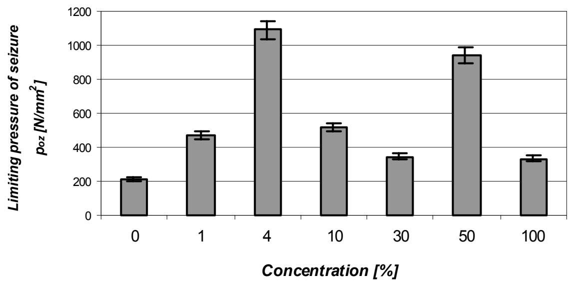


Fig. 7. Limiting pressure of seizure p_{oz} versus concentration of water solutions of ethoxylated sorbitan monostearate

After analyzing seizure load one can see that for low concentration (up to 10 %) the increment of content of ESMS in water significantly increases the investigated quantities. For higher concentration the increment of p_{oz} was not observed. As far as scuffing load is concerned, the increment of concentration of ESMS above 10 % causes decrease of the measured quantities. For pure ester, however, the increment of p_t was observed.

Dependence of limiting pressure of seizure on ESMS concentration is different from the ones discussed up to now. The highest values were obtained for 4 % and 50 % solutions (Fig. 7).

3.3. Antiseizure properties of ethoxylated sorbitan monooleate water solutions

For water solutions of ESMO, highest values of seizure load were observed for 1 %, 4 % and 10 % solutions. The obtained results are presented in Fig. 8. In the case of limiting pressure of seizure one should pay attention to the fact that the analyzed parameter deteriorates for 30 % solution.

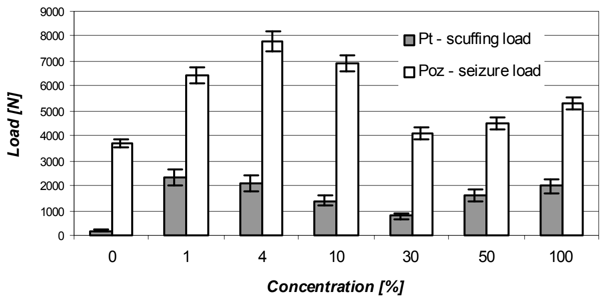


Fig. 8. Scuffing load P_t and seizure load P_{oz} versus concentration of water solutions of ethoxylated sorbitan monooleate

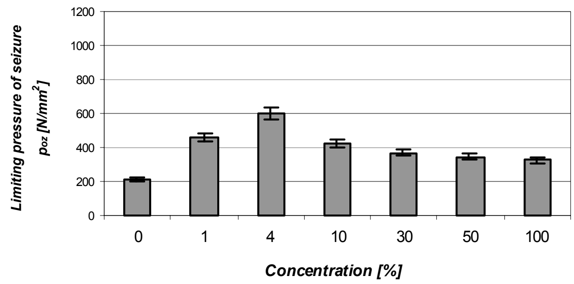


Fig. 9. Limiting pressure of seizure p_{oz} versus concentration of water solutions of ethoxylated sorbitan monooleate

After analysis of Fig. 9 one can see that increment of limiting pressure of seizure goes with increment of concentration (up to 4 %). Further increasing of additive concentration causes decreasing of the analyzed parameter.

4. DISCUSSION

On the basis of the performed tests one can see that ethoxylated sorbitan esters have considerable viscosity. Viscosity of 1 % solution is 10 times higher than viscosity of water. It is a premise that for these concentrations the structure of the solution is different from the perfect solution. One can suppose that micelles which have various shapes arise and this fact influences viscosity. Along with concentration, increment of viscosity is observed. The increment is 1000 times higher for ESML solutions and 50000 – 80000 times for ESMS and ESMO solutions. This fact shows that liquid crystalline structures arise. It is confirmed by polarization micrographs for 50 % ESMS and ESMO solutions. Very high viscosity of ESMS and ESMO water solutions and polarization micrographs are premises to state that a hexagonal structure is formed. It is well known that lyotropic liquid crystals occur in lamellar form for high concentrations. That leads to a significant decrease of viscosity.

Structure of a lamellar phase can improve tribological properties. Slip planes which can modify motion resistance in the direction of motion are formed. On the other hand, the layer is strongly connected to the base and it provides high mechanical strength for perpendicular forces.

Concentration of additive is higher in the surface phase than in the bulk phase because of strong interaction between applied chemical substances and surface of friction couple. It can be expected that for concentration about 1 % the surface phase is completely filled with the additive. That is why, for 1 % solutions, high increment of the measured values was observed. For example, the scuffing load for all the solutions was 11 – 23 times higher than for pure solvent. Comparison of the applied compounds reveals that at low concentrations ESMS and EMSO have most favorable properties – for 1 % solutions the scuffing load was more than 2000 N. Further increasing of the concentration (above 10 %) caused reduction of P_t.

For seizure load a type of compound was meaningless. A significant increase in the measured value was observed for concentrations from 1 % to 10 %.

As far as the limiting pressure of seizure is concerned, 1 % addition of particular compounds to water increased the measured parameter more than two times.

The existence of extrema of measured quantities as functions of concentrations is particularly interesting. It can be explained by existence of different mesophases in the surface and bulk phases. For ESMS highest values were observed at 10 % concentration, whereas for ESMO, at 4 %. The best antiseizure properties for ESMS were observed for 4 % and 50 % solutions.

Possibility of creation of various liquid crystalline structures as well as energy of additive - surface interaction significantly influences seizure. It can be confirmed by the existence of extrema, even at low concentrations.

5. CONCLUSION

On the basis of the presented results we can say that:

- Addition of ethoxylated sorbitan esters to the water improves its antiseizure properties.
- A considerable influence of additive concentration on tribological properties was observed.
- The type of applied additives has an effect on measured values.

Acknowledgements

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REFERENCES

1. **Fuller, S., Li, Y., Tiddy, T. J., Wyn-Jones, E., Arnell, R. D.** Formulation of Lyotropic Lamellar Phases of Surfactants as Novel Lubricants *Langmuir* 11 1995: pp. 1980 – 1983.
2. **Lee, H. S., Winoto, S. H., Winer, W. O., Chiu, M., Friberg, S. E.** Film Thickness and Frictional Behavior of Some Liquid Crystals in Concentrated Point Contacts *Tribology and the Liquid Crystalline State*, *American Chemical Society*, Washington 1990: pp. 113 – 125.
3. **Lockwood, F. E., Benchaita, M. T., Friberg, S. E.** Study of Lyotropic Liquid Crystals in Viscometric Flow and Elastohydrodynamic Contact *ASLE Transactions* 30 1987: pp. 539 – 548.
4. **Kumar, K., Shah, D. O.** Effect of Liquid-crystalline Structures on Lubrication of Aluminium Surfaces *Tribology and the Liquid Crystalline State, American Chemical Society* Washington 1990: pp. 91 – 100.
5. **Boschkova, K., Elvesjo, J., Kronberg, B.** Frictional Properties of Lyotropic Liquid Crystalline Mesophases at Surface *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 166 2000: pp. 67 – 77.
6. **Friberg, S., Ward, A., Gunsel, S., Lockwood, F.** Lyotropic Liquid Crystals in Lubrications *Tribology and the Liquid Crystalline State, American Chemical Society* Washington 1990: pp. 101 – 112.
7. **Ratoi, M., Spikes, H. A.** Lubricating Properties of Aqueous Surfactant Solutions *Tribology Transactions* 42 1999: pp. 479 – 486.
8. **Wei, J., Xue, Q.** Effects of Surfactants on the Tribological Properties of a Cr_2O_3 *Wear* 162 – 164 1993: pp. 229 – 233.
9. **Wei J., Xue Q.** The Friction and Wear Properties of Cr_2O_3 Coating with Aqueous Lubrication *Wear* 199 1996: pp. 157 – 159.
10. **Sułek, M. W., Wasilewski, T.** Influence of Alkyl Polyglycosides on Lubricating Properties of Water and Glycerin *Inżynieria Powierzchni* 4 2001: pp. 52 – 58 (in Polish).
11. **Sułek, M. W., Wasilewski, T.** Influence of the Structure of Ethoxylated Sodium Lauryl Sulfate Water Solutions on their Tribological Properties *Zagadnienia Eksploatacji Maszyn* 129 (1) 2002: pp. 35 – 47 (in Polish).
12. **Sułek, M. W., Wasilewski, T.** Tribological Properties of Lubricants, which are Containing Alkyl Polyglycosides *Tribologia* 2 2002: pp. 741 – 753 (in Polish).
13. **Sułek, M. W., Wasilewski, T.** Tribological Properties of Sorbitan's Esters Applied as Lubricant Additives *Tribologia* 3 2001: pp. 447 – 461 (in Polish).
14. **Piekoszewski, W., Szczerek, M., Tuszyński, W.** The Action of Lubricants Under Extreme Pressure Conditions in a Modified Four-Ball Tester *Wear* 249 2001: pp. 188 – 193.

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