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## THE EFFECT OF THE FORMATION OF POLYMER/SURFACTANT COMPLEXES ON SELECTED TRIBOLOGICAL PROPERTIES OF THEIR AQUEOUS SOLUTIONS

### WPLYW TWORZENIA KOMPLEKSÓW POLIMERÓW Z SURFAKTANTAMI NA WYBRANE WŁAŚCIWOŚCI TRIBOLOGICZNE ICH WODNYCH ROZTWORÓW

<b>Key words:</b>	lubricating properties, motion resistance, antiseizure properties, aqueous solutions, polymer/surfactant complexes, sodium lauryl sulfate, polyvinylpyrrolidone.
<b>Abstract</b>	Aqueous solutions of sodium alkyl sulphate (surfactant) and polyvinylpyrrolidone (polymer) whose physicochemical properties, including complexing ability, have been widely described in the literature were proposed as a model lubricant. It has been assumed that aqueous solutions of these compounds will favourably modify lubricating properties of water under high load conditions. For this purpose, measurements were made on a four-ball apparatus (T-02 Tester) for aqueous solutions of these compounds. Two kinds of tests were carried out: at constant loads (2, 3, and 4 kN) and variable loads within the range of 0 to 7.2 kN. Unexpectedly, high decreases in motion resistance and wear as well as an increase in antiseizure properties were found in relation to water as a base. The results obtained are so promising that solutions with an optimized composition can find practical applications. The surprisingly high effectiveness of the additives used results from the formation of surfactant/polymer complexes. These adducts adsorb at the interface, and, under friction conditions, they form a lubricant film capable of carrying high loads.
<b>Słowa kluczowe:</b>	właściwości smarne, opory ruchu, właściwości przeciwzatarciowe, wodne roztwory, kompleksy polimerów z surfaktantami, laurylosiarczan sodu, poliwinylpirolidon.
<b>Streszczenie</b>	Jako modelową substancję smarową zaproponowano wodne roztwory alkilosiarczanu sodu (surfaktant) i poliwinylpirolidonu (polimer), których właściwości fizykochemiczne, w tym zdolność do kompleksowania, zostały szeroko opisane w literaturze. Postawiono tezę, że wodne roztwory tych związków będą korzystnie modyfikowały właściwości smarne wody w warunkach wysokich obciążeń. W tym celu dla wodnych roztworów tych związków wykonano pomiary na aparacie czterokulowym (Tester T-02). Przeprowadzono 2 rodzaje testów: przy stałych obciążeniach (2, 3, 4 kN) oraz przy zmiennym obciążeniu w przedziale zmienności od 0 do 7,2 kN. Stwierdzono nieoczekiwane duże obniżenie oporów ruchu i zużycia oraz wzrost właściwości przeciwzatarciowych w odniesieniu do wody jako bazy. Uzyskane wyniki są na tyle obiecujące, że roztwory o zoptymalizowanym składzie mogą znaleźć zastosowanie praktyczne. Niespodziewanie wysoka efektywność stosowanych dodatków jest konsekwencją tworzenia kompleksów surfaktanta z polimerem. Addukty te adsorbują na granicy faz, a w warunkach tarcia tworzą film smarny zdolny do przenoszenia wysokich obciążeń.

## INTRODUCTION

The results of studies on aqueous solutions of surface active agents (surfactants) have shown that they may be model lubricating substances and, after introducing

additives, they can find practical applications [L. 1–16, 24]. Recently, it has been found that polymer additives have an important beneficial effect on physicochemical, tribological, and functional properties of these solutions [L. 2, 3, 9, 24, 25].

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As the results of our own research and literature research show, polymers form complexes with surfactants in aqueous solutions [L. 2, 4, 9, 18, 19, 25, 26]. Based on an analysis of those results, a hypothesis was proposed that indicates a dominant impact of these structures on tribological and functional properties of lubricating substances. Additionally, proposals were presented regarding the action mechanism of additives in the friction zone. So far, the use of this type of solutions in lubrication technology has not been proposed. Some tribological tests were carried out for various combinations of polymers with surfactants in order to verify the thesis presented. This paper presents the results obtained for aqueous solutions of sodium lauryl sulphate (SLS) and polyvinylpyrrolidone (PVP90). The formulated conclusions will be verified in further research for other polymers and surfactants and the results will be published.

#### SELECTED PHYSICOCHEMICAL PROPERTIES OF AQUEOUS SOLUTIONS OF LAURYL SULFATE WITH VINYLPIRROLIDONE

Numerous literature reports indicate that polymers form complexes with surfactants [L. 2, 3, 9, 18, 19, 25, 26]. The most stable ones are those formed with anionic surfactants, while those with cationic and anionic surfactants are significantly weaker. Various kinds of interactions between polymers and surfactants can be expected. The most common ones are electrostatic, hydrophobic, and dipole interactions, or those through hydrogen bonds. The mass of the polymer is significantly higher than that of the surfactant. For example, the molecular mass of PVP90 is 10,000, while the molecular mass of SDS is 305, so the mass of the polymer is ca. 33 times higher and it fills a much larger space. For surfactants, it is a specific phase boundary at which adsorption takes place.

As a result of the formation of polymer/surfactant complexes, the solutions gain some individual properties different from those observed in binary solutions. Changes in surface tension  $\sigma$  as a function of surfactant concentration ( $c_s$ ) are particularly interesting. A schematic illustration of these changes is shown in Fig. 1.

It does not show real functional dependencies but only the location of individual characteristic points. In Fig. 1, the continuous line represents the dependence of surface tension for surfactant solutions, and the broken line represents the relationship of surface tension for solutions of surfactants with the polymer.

Individual quantities are as follows:

- CAC – critical concentration of polymer/surfactant aggregate formation,
- CMC – critical micelle concentration in surfactant solution, and

- CMC' – critical micelle concentration of surfactant in polymer/surfactant solution.

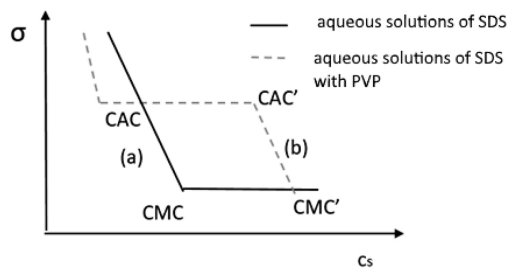


Fig. 1. Schematic dependence of surface tension  $\sigma$  as a function of surfactant concentration ( $c_s$ ) for aqueous solutions of polymers with surfactants

Rys. 1. Schematyczna zależność napięcia powierzchniowego  $\sigma$  w funkcji stężenia surfaktanta ( $c_s$ ) dla wodnych roztworów polimerów z surfaktantami

The process of the formation of polymer/surfactant complexes was finished at the CAC' point. Studies show that solutions of polymer/surfactant complexes may exhibit lower surface tension compared to surfactant solutions. As a result, the complex being formed may show a higher surface activity.

The analysis of surface tension confirms the formation of polymer/surfactant complexes [L. 18, 25, 26]. The dependence  $\sigma(cSLS)$  is monotonic and a drop in surface tension can be observed with an increase in surfactant concentration. The correlations between the  $\sigma$  values for SLS solutions as well as SLS and PVP90 solutions are as expected. Aggregates of PVP with SLS monomers form with SLS concentration below CMC corresponding to CAC concentration. For 1 mM PVP solutions, the  $\sigma$  values even for high SLS concentrations are relatively high (ca. 33 mN/m). These results may indicate that complete complexing of the polymer with the surfactant did not occur. Additionally, this hypothesis can be confirmed by the fact that relatively low values of surface tension ( $\sigma = 29$  mN/m) were reached by solutions with 0.01 mM PVP concentration. Due to a lower number of active centres (fewer polymer molecules), one can expect complete saturation of possible bonds of surfactant with the polymer. The 29 mN/m value is lower than the values obtained for the SDS solution. Additionally, an increase in the value of surface tension can be observed with an increase in PVP concentration and with constant SDS concentration. This dependence may point to the competitiveness of interactions of SDS with PVP compared to the interface.

Additionally, the wettability of steel by three-component solutions decreases as a function of lauryl sulphate concentration reaching the lowest values at the lowest PVP concentration [L. 18, 25, 26]. With an increase in PVP concentration, the wettability angle increases and wettability decreases. This dependence is monotonic for concentrations comparable with CMC

concentration for SDS solutions. In this concentration range, aggregates form with various saturations of active polymer centres. The highest saturation is expected for lower PVP concentrations. Therefore, the highest wettability of steel by solutions is observed at these concentrations.

### TRIBOLOGICAL PROPERTIES OF POLYVINYLPIRROLIDONE SOLUTIONS WITH SODIUM ALKYL SULFATE

Section 2 presents the results of measurements of changes in surface tension and the wettability of aqueous solutions of PVP and/or SLS. On their basis and the results of other authors, the presence of complexes of sodium alkyl sulphate with polyvinyl pyrrolidone was confirmed in the solutions which, depending on SDS concentration, can occur in equilibrium with monomers or possibly surfactant micelles. The low surface tension values in three-component solutions may indicate effective adsorption of complexes on steel surfaces and, as a result, the formation of a lubricant film under friction conditions. The confirmation of this thesis was searched for experimentally by determining the tribological properties of selected solutions. The measurements were carried out using a T-02 tribometer for which technical solutions and measurement methods were developed at the Institute for Sustainable Technologies (PN-76C-04147).

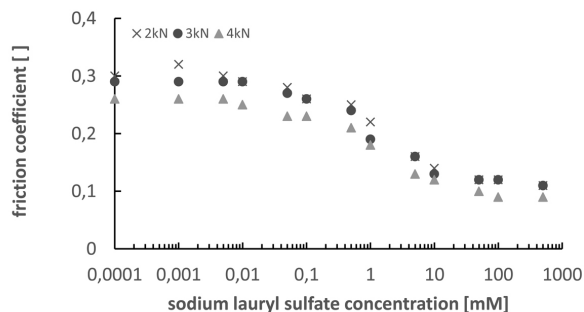
#### Tribometer T-02

The tests were carried out at a constant load (2, 3, and 4 kN) and a variable load (from 0 to 7.2 kN) with a load increase rate of 409 N/s. The measurement methodology was described in detail in the literature [L. 28].

#### Tests at constant load (Tribometer T-02).

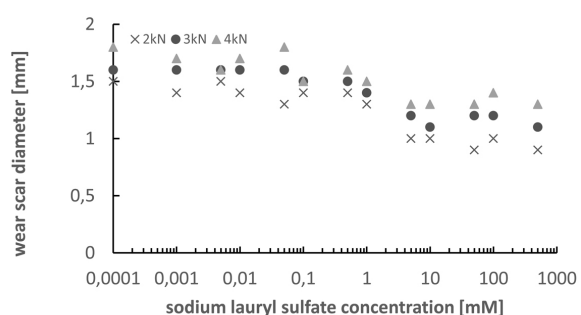
Friction coefficient ( $\mu$ ) and wear scar diameter ( $d$ ) of 1 mM solutions of polyvinylpyrrolidone (PVP) and sodium alkyl sulphide (SDS) were measured as a function of SDS concentration. The measurement conditions were as follows: T-02 apparatus, rotational spindle velocity 200 rpm, test duration 900 s, and loads 2, 3, and 4 kN. The results obtained are presented, respectively, in Fig. 2 ( $\mu(c_{\text{SDS}})$ ) and in Fig. 3 ( $d(c_{\text{SDS}})$ ).

Tribological systems did not undergo seizure in the presence of the solutions tested. This is the effect of the additives (SDS and PVP) as, in the presence of water, the tribological system underwent seizure at loads of 3 and 4 kN. However, at the load of 2 kN, the  $\mu$  and  $d$  values for water were, respectively, 0.47 and 1.8 mm. The addition of PVP to water improved friction conditions, and the system did not undergo seizure. The friction coefficient values were 0.29, 0.26, and 0.19, and wear scar diameters were 1.3, 1.5, and 1.7 for loads of 2, 3, and 4 kN, respectively. A characteristic in the



**Fig. 2. Dependence of friction coefficient as a function of SLS concentration in aqueous solutions of PVP90. Friction coefficients for 1 mM aqueous solutions of PVP90 are: 0.29 (2 kN), 0.26 (3 kN), 0.19 (4 kN)**

Rys. 2. Zależność współczynnika tarcia w funkcji stężenia SLS w wodnych roztworach PVP90. Współczynnik tarcia dla 1 mM wodnych roztworów PVP90 wynosi: 0,29(2 kN), 0,26 (3 kN), 0,19(4 kN)



**Fig. 3. Dependence of wear scar diameter as a function of SLS concentration in aqueous solutions of PVP90. Wear scar diameters for 1 mM aqueous solutions of PVP90 are: 1.3 mm (2 kN), 1.5 mm (3 kN), 1.7 mm (4 kN)**

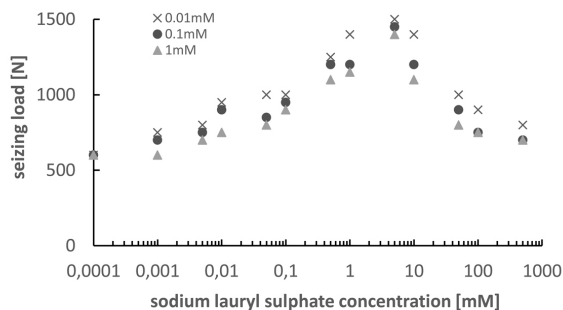
Rys. 3. Zależność średnicy szczytu kulki w funkcji stężenia SLS w wodnych roztworach PVP90. Średnice szczytu kulki dla 1 mM wodnych roztworów PVP90 wynoszą: 1,3 mm (2 kN), 1,5 mm (3 kN), 1,7 mm (4 kN)

course of the  $\mu(c_{\text{SLS}})$  and  $d(c_{\text{SLS}})$  dependencies is an intense decrease in these quantities followed by stabilization or a small increase (Figs. 6 and 7). An intense reduction in motion resistance and wear starts from a value of above 1 mM in the concentration range corresponding to critical concentration of complex formation (CAC) [L. 23] and ends in the 8–10 mM which is the concentration range corresponding to SDS micelle formation in the bulk phase.

#### Tests at a variable load (Tribometer T-02)

The values being measured are seizing load ( $P_v$ ), seizure load ( $P_{oz}$ ), wear scar diameter ( $d_{oz}$ ), and limiting pressure of seizure ( $p_{oz}$ ). These quantities were described and interpreted [L. 28], and their dependencies on concentrations of polyvinylpyrrolidone

and sodium lauryl sulphate (SLS) are shown in **Figs. 4–7**. Measurement conditions are as follows: T-02 apparatus, test at an increasing load, test duration 18 s, and load accretion 409 N/s.

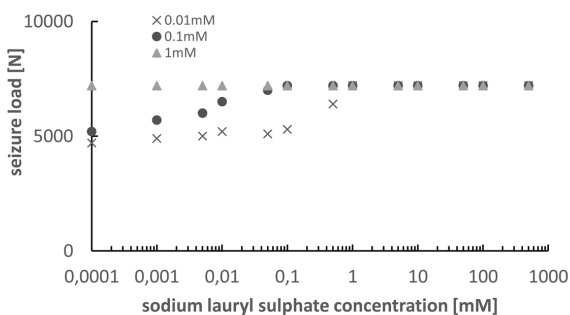


**Fig. 4. Dependence of seizing load as a function of SLS concentration in PVP90 solutions**

Rys. 4. Zależność obciążenia zacierającego w funkcji stężenia SLS w roztworach PVP90

There is no evident impact of PVP concentration on the measured value of seizing load ( $P_t$ ), which, for various values of PVP concentrations (0.01, 0.1, 1 mM), takes the value of about 600 N. Thus, PVP solutions show about three times greater ability to form a lubricant film protecting against wear compared to water (ca. 200 N). The maximum Pt values for three-component solutions are taken by solutions for SDS concentrations of 1 to 10 mM, and they are even two and a half times higher than those determined for PVP solutions. This concentration range (1–10 mM) can be compared with the concentration range from CAC to CMC (**Fig. 1**). A slight decrease in seizing load can be observed with an increase in PVP concentration.

Under high-pressure conditions, both aqueous solutions of polyvinylpyrrolidone, sodium lauryl sulphate and three-component solutions well protect friction pairs against seizure (**Fig. 5**).

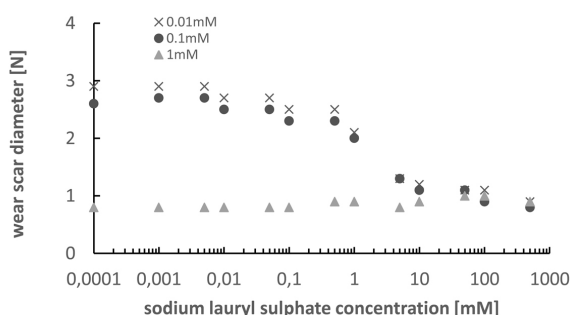


**Fig. 5. Dependence of seizure load as a function of SLS concentration in aqueous solutions of PVP90**

Rys. 5. Zależność obciążenia zatarcia w funkcji stężenia SLS w wodnych roztworach PVP90

Seizure load increases for polyvinylpyrrolidone solutions with an increase in concentration from 4.7 kN ( $c_{PVP} = 0.01$  mM) to 7.2 kN ( $c_{PVP} = 1$  mM). After adding sodium lauryl sulfate to 0.01 mM PVP solutions, there occurs an increase in  $P_{oz}$  which takes the maximum value at  $c_{SDS} = 1$  mM. Analogous to 0.1 mM PVP solutions, the 7.2 kN is obtained by solutions at 0.01 mM SDS concentration. However, 1 mM PVP solutions take the maximum  $P_{oz}$  values already at the lowest SDS concentration. It can be stated that, in spite of relatively low surface activity of PVP at  $c_{PVP} \approx 1$  mM concentrations, the polymer forms an adsorption layer, which forms a stable lubricant film at high loads. The effect of high load carrying can also be obtained at about 100 times lower PVP concentrations if SLS is introduced as the other additive complexing with PVP. This effect results from interaction with the base of the SLS – PVP adduct.

The character of changes observed for variations in wear scar diameter ( $d_{oz}$ ) as a function of alkyl sulphate concentration ( $c_s$ ) is close to the dependence  $P_{oz}$  ( $c_{SLS}$ ,  $c_{PVP}$ ) (**Fig. 6**).

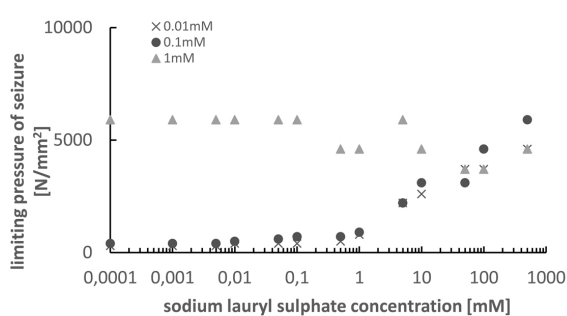


**Fig. 6. Dependence of wear scar diameter as a function of SLS concentration in aqueous solutions of PVP90**

Rys. 6. Zależność średnicy śladu zużycia w funkcji stężenia SLS w wodnych roztworach PVP90

Polyvinylpyrrolidone solutions do not reach the  $d_{oz}$  value in the 0.9–1.0 mm range until the concentration of 1 mM. Comparable wear scar diameter values can also be observed at the 10 mM SLS concentration even for the lowest PVP concentrations (**Fig. 6**). The alternative for high PVP concentration is then the use of a polymer–surfactant system, which is capable of forming complexes in aqueous solutions. Similarly as in the case of dependencies of other quantities ( $P_t$ ,  $P_{oz}$ ) as a function of SDS concentration, significant changes can be observed in the 1–10 mM concentration range, which can be associated with the critical concentrations CAC and CMC.

The results of the high  $P_{oz}$  values and low  $d_{oz}$  values are high values of the limiting pressure of seizure (**Fig. 7**).



**Fig. 7. Dependence of limiting pressure of seizure as a function of SLS concentration in aqueous solutions of PVP90**

Rys. 7. Zależność granicznego obciążenia zatarcia w funkcji stężenia SLS w wodnych roztworach PVP90

## DISCUSSION OF THE RESULTS AND SUMMARY

Tribological tests were carried out for a model lubricating substance in the form of aqueous solutions of sodium lauryl sulphate (SDS) and polyvinylpyrrolidone (PVP90). Solutions with various contents of individual components (SLS, PVP) were tested at high loads of the order of kN. The loads applied were both constant and variable.

The systems did not undergo seizure in tests at three different constant loads (2, 3, and 4 kN) in a four-ball apparatus (Figs 2 and 3) containing aqueous solutions of PVP and SLS as lubricating media. PVP solutions demonstrated similar properties with both friction coefficients and wear scar diameter ( $d$ ) being considerably higher. Moreover, tribological studies carried out using a T-02 tester at a variable load (409 N/s) gave positive results when aqueous solutions of PVP and SLS were the lubricating substance. The ability to form a stable lubricant film characterized by

seizing load ( $P_t$ ) is very high and the  $P_t$  values reach 1.5 kN. This is over seven-fold higher than the one for water. The system carries loads to the maximum value (7.2 kN) available in the T-02 tester. Up to that boundary load ( $P = 7.2$  kN), wear is relatively low – ca. 0.9 mm. High values of limiting pressure of seizure ( $p_{oz}$ ) result from carrying the highest loads (7.2 kN) and low wear ( $d_{oz} = 0.9$  mm). The limiting pressure of seizure reaches the values of even up to about 6000 N/mm<sup>2</sup>.

Summing up, the results of the tests carried out on the T-02 tribometer for various quantities and kinds of loads (constant and variable) indicate that solutions of PVP+SLS show beneficial properties which imply their practical applications. The tribological characteristics of the three-component solutions are more beneficial than those of polymer solutions. It has also been found that SLS concentrations strongly affect tribological properties. An analysis of tribological properties of solutions with polymers and surfactants was carried out to explain and interpret the results obtained. The comparison of the results of physicochemical studies (changes in surface tension and wettability) with tribological results indicates that polymer/surfactant complexes play an important role in reducing motion resistance and wear as well as in their high ability to protect against the seizure of the system. The existence of these adducts has been proven and the leading role is played by hydrophobic interactions.

The formation of complexes in aqueous solutions of PVP and SLS and their adsorption on the surface of mating friction pairs have a significant influence on the determined tribological characteristics. Under friction, the adsorption layer turns into a lubricant film protecting the friction couples against excessive wear and seizing and minimizes motion resistance. This is confirmed by beneficial changes in tribological quantities in the range of SDS concentrations in which the ( $C_{SDS} > CAC$ ) complexes are formed.

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